Electrochemical Synthesis of Cobalt Complexes with 4-Methyl-*N*-(2-pyridylmethyl)benzenesulfonamide (HL) − Crystal Structures of HL, $[Co^{II}L_2]$ and $[Co^{III}L_2L^o]$ $[L^o = \{HNC(CH_3)\}_2C(CN)]$

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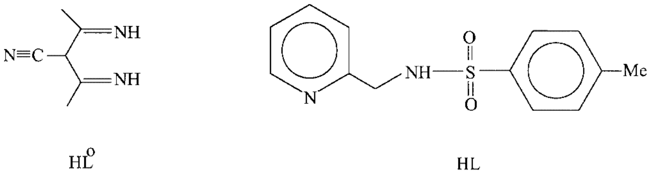
Electrochemical oxidation of cobalt in a solution of 4-methyl-*N*-(2-pyridylmethyl)benzenesulfonamide (HL, **1**) in acetonitrile afforded the compounds $[Co^{II}L_2]$ (**2**) or $[Co^{III}L_2L^o]$ (**3**). When 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) was added to the electrolytic phase, $[Co^{II}L_2bipy]$ (**4**) and $[Co^{II}L_2phen]$ (**5**) were obtained. The crystal structures of HL (**1**), $[Co^{II}L_2]$ (**2**) and $[Co^{III}L_2L^o]$ (**3**) were determined by X-ray diffraction techniques. The compound $[Co^{II}L_2]$ is mononuclear and has a distorted tetrahedral $[CoN_4]$ geometry, with each amide ligand acting as an anionic $(N_{amide}N_{py})$ bidentate ligand. In the monomeric complex $[Co^{III}L_2L^o]$ the cobalt atom is in a distorted octahedral $[CoN_6]$ environment defined by the amide and pyridyl nitrogen atoms of two L^- anionic ligands and the two nitrogen atoms of the NH groups of a new anionic ligand L^o, which is formed by trimerisation of three acetonitrile molecules in the electrolytic cell. The electronic, IR and FAB spectra of the compounds are discussed.

Introduction

Electrochemical procedures have been widely used for the synthesis of metal complexes, especially when the ligands have weakly acidic organic donor groups. It is well known that metal complex formation by substitution of the amide proton by a metal ion is not an easy process.[1] However, the presence of an additional donor atom in the molecule allows the formation of a stable five- or six-membered chelate ring with the metal ion[2] and this situation may facilitate the complexation process. In addition, the presence of a tosyl group in the amide increases the acidity of the amide hydrogen atom, making the formation of the anionic ligand easier.[3]

The work described here is a continuation of our previous studies on metal complexes with ligands containing a pyridyl ring and a tosylamide group.[4] This paper describes the preparation of the ligand [4-methyl-*N*-(2-pyridylmethyl)benzenesulfonamide] (HL, **1**) (Scheme 1), and the cobalt complexes $[Co^{II}L_2]$ (**2**), $[Co^{II}L_2L']$ [where L′ is 2,2′-bipyridine (bipy) (**4**), 1,10-phenanthroline (phen) (**5**) and $[Co^{III}L_2L^o]$ (**3**), where L^o (Scheme 1) represents the anionic form of an additional ligand formed during the electrochemical process by trimerisation of three molecules of acetonitrile.



Scheme 1

Results and Discussion

The ligand [4-methyl-*N*-(2-pyridylmethyl)benzenesulfonamide] (HL) was prepared by a standard procedure, by treatment of 2-(aminomethyl)pyridine with *p*-toluenesulfonyl chloride in the presence of base. An interesting feature of the ^1H NMR spectrum of the ligand is the signal at $\delta = 11.6$ ppm for the NH proton in $CDCl_3$; for simple sulfonamides of the form $RSO_2NH{-}Ar$ this resonance normally appears at $\delta \approx 7$ ppm. The observed difference was probably due to the presence in solution of an intramolecular hydrogen bonding interaction between the NH group and the pyridine nitrogen atom. The same explanation can also be put forward to explain the very lowfield resonance of the OH proton in the case of the salicylaldimines.

Molecular Structure of the Ligand HL (1)

The molecular structure of [HL] is shown in Figure 1, together with the adopted atomic numbering scheme. Selected bond lengths and angles are given in Table 1.

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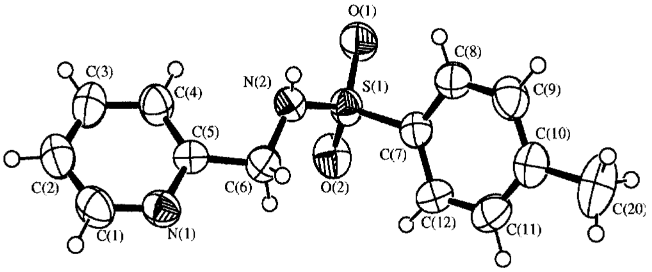


Figure 1. Perspective view of HL (50% probability displacement ellipsoids)

Table 1. Selected bond lengths [Å] and angles [°] for the ligand [HL]

S(1)−O(2)	1.419(4)	S(1)−O(1)	1.432(4)
S(1)−N(2)	1.603(5)	S(1)−C(7)	1.763(5)
N(1)−C(1)	1.341(7)	N(1)−C(5)	1.344(6)
N(2)−C(6)	1.447(7)	C(1)−C(2)	1.358(9)
C(2)−C(3)	1.357(10)	C(3)−C(4)	1.388(8)
C(4)−C(5)	1.372(8)	C(5)−C(6)	1.515(7)
C(7)−C(12)	1.389(8)	C(7)−C(8)	1.394(8)
C(8)−C(9)	1.377(9)	C(9)−C(10)	1.372(9)
C(10)−C(11)	1.387(9)	C(10)−C(20)	1.505(8)
C(11)−C(12)	1.3376(9)		
O(2)−S(1)−O(1)	119.7(3)	O(2)−S(1)−N(2)	107.5(3)
O(1)−S(1)−N(2)	106.1(3)	O(2)−S(1)−C(7)	108.1(3)
O(1)−S(1)−C(7)	107.5(3)	N(2)−S(1)−C(7)	107.4(3)
C(1)−N(1)−C(5)	117.3(5)	C(6)−N(2)−S(1)	122.5(4)
N(1)−C(1)−C(2)	124.5(6)	C(3)−C(2)−C(1)	117.7(6)
C(2)−C(3)−C(4)	120.0(7)	C(5)−C(4)−C(3)	118.9(7)
N(1)−C(5)−C(4)	121.6(5)	N(1)−C(5)−C(6)	115.1(5)
C(4)−C(5)−C(6)	123.3(5)	N(2)−C(6)−C(5)	111.4(5)
C(12)−C(7)−C(8)	120.7(6)	C(12)−C(7)−S(1)	120.9(5)
C(8)−C(7)−S(1)	118.4(5)	C(9)−C(8)−C(7)	118.7(7)
C(10)−C(9)−C(8)	122.1(7)	C(9)−C(10)−C(11)	117.9(6)
C(9)−C(10)−C(20)	121.5(7)	C(11)−C(10)−C(20)	120.7(7)
C(12)−C(11)−C(10)	122.2(7)	C(11)−C(12)−C(7)	118.4(6)

The bond lengths and bond angles of the phenyl and pyridine rings are similar to those found in other pyridylbenzenesulfonamide ligands.[5−9] The C(6)−N(2) and S(1)−N(2) distances [1.447(7) and 1.603(5) Å] are very close to those observed in *N*-(*p*-tolylsulfonyl)benzylamine [1.475(3) and 1.619(2) Å].[10]

The phenyl and pyridine rings are almost flat, with the maximum deviation of any atom from the best least-squares planes being 0.010(5) and 0.011(4) Å, respectively. The carbon atom C(20) and the sulfur atom S(1) lie approximately in the plane of the phenyl ring to which they are bound [deviation of 0.022(10) Å for C(20) and 0.019(7) Å for S(1)]. Atom C(6) is also out of the plane of the pyridine ring to which it is bound [0.102(10) Å]. The interplanar angle between the phenyl and pyridine rings is 55.7°.

The crystal structure is completed by half a water molecule, which is associated with the ligand molecules through intermolecular hydrogen bonds. Hydrogen bonds exist between the pyridine nitrogen atoms of two ligand molecules and the oxygen atom of the water molecule. In addition, the oxygen atom of the water molecule is involved in a hydrogen bond with the amide nitrogen atoms of two other neighbouring ligands. Therefore, infinite hydrogen bonded chains of ligand and water molecules are formed in this system (Table 2).

Table 2. Hydrogen bonds in the ligand

Atoms: A···HD	*d*(A···H)	*d*(H−D)	*d*(A···D)	< AHD
O3···H(20)−N(2)	2.168(5)	0.74(5)	2.880(7)	161.77(6)
N(1)#···H(31)−O(3)	1.824(7)	0.97(7)	2.775(6)	166.24(6)

Cobalt Complexes

The cobalt complex [$Co^{II}L_2$] and its adducts with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) − [$Co^{II}L_2$(bipy)] and [$Co^{II}L_2$(phen)], respectively − were prepared in good yield by the simple one-step electrochemical method described below. In all cases, the product formed was separated by filtration as a crystalline product. In addition, all of the compounds were air-stable and moderately soluble in organic solvents such as ethanol or chloroform.

The values of the electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, were all close to 0.5 mol·F^{-1}, irrespective of the presence or absence of additional ligands. This fact, in conjunction with the evolution of hydrogen at the cathode, is compatible with the following mechanism:

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

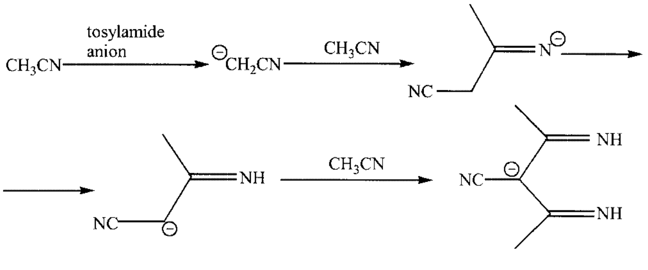
Anode: $Co + 2\ L^- \longrightarrow [Co^{II}L_2] + 2\ e^-$

or, when an additional neutral ligand (L' = bipy or phen) is added:

Anode: $Co + 2\ L^- + L' \longrightarrow [Co^{II}L_2L'] + 2\ e^-$

When the electrochemical oxidation of cobalt metal in an acetonitrile solution of the amide ligand was carried out at a much higher voltage than in the previous case, the compound [$Co^{III}L_2L^o$] was formed. In this compound, besides the deprotonated amide ligands, a new ligand, formed by trimerisation of three acetonitrile molecules, appears in the coordination sphere of the metal ion.

The trimerisation of acetonitrile can be viewed as the result of a tandem reaction catalysed by the nucleophilic attack of a tosylamide anion, formed during the electrochemical reaction, on an acetonitrile molecule, as shown in Scheme 2.



Scheme 2

It is most probable that these reactions occur in the coordination sphere of the metal ion, given the fact that they do not occur in its absence. The occurrence of this process may be ascribed to the increased sensitivity of the acetonitrile molecule to nucleophilic attack as a result of coordination to the metal ion. This reaction can be considered as the intramolecular version of the Thorpe−Ziegler reaction.

The CH_3CN trimerisation process is not without precedent. It has previously been observed when MMe_3 (M = Al, Ga or In) was boiled for 24−72 h at 60−65 °C in acetonitrile in the presence of cesium halides ($X = F^-, Cl^-, Br^-$) to give $[CH_3M\{HNC(CH_3)\}_2C(CN)]$.[11,12]

Molecular Structure of $[Co^{II}L_2]$ (2)

The molecular structure of $[Co^{II}L_2]$ is shown in Figure 2, along with the adopted atomic numbering scheme. Selected bond lengths and angles are listed in Table 3. The structure of the complex consists of mononuclear units in which a tetracoordinated cobalt atom is bound to both nitrogen atoms of two bidentate monoanionic ligands in a distorted tetrahedral arrangement. Two different Co−N bond lengths are observed: the bonds involving amide nitrogen atoms [1.926(4), 1.946(4) Å] are significantly shorter than those involving pyridine nitrogen atoms [2.028(4), 2.040(4) Å]. These values are similar to those found in other cobalt compounds containing both anionic and neutral nitrogen donor atoms, such as in the tetrahedral complex [2-tosylamino(2′-pyridyl)anilinato]cobalt(II) [$Co-N_{amide}$, 1.959(13) Å][13] or in the cobalt(II) complex with the ligand obtained by the reaction between 2-(2-aminophenyl)pyridine with *p*-toluenesulfonyl chloride[3] [$Co-N_{amide}$ 1.960(2), 1.967(2) Å; $Co-N_{pyridine}$ 2.041(2), 2.043(2) Å]. The tetrahedral environment of the cobalt atom is distorted due to the small bite required by N−Co−N = 81.37(16)−82.08(16)°, which also results in secondary deviation of the other perinuclear angles from the ideal values of 109°. Each five-membered chelate ring lies in a plane with the maximum deviation of any atom from this plane being 0.0004 and 0.0165 Å. The two planes are nearly perpendicular, with a dihedral angle of 82.11°. In each ligand the phenyl and pyridine rings are planar.

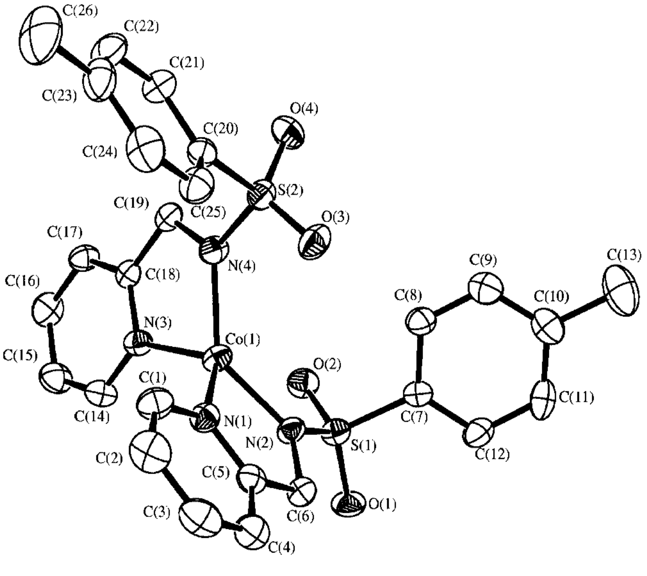


Figure 2. Perspective view of $[Co^{II}L_2]$ (50% probability displacement ellipsoids)

Table 3. Selected bond lengths [Å] and angles [°] for the complex $[Co^{II}L_2]$

Co(1)−N(2)	1.926(4)	Co(1)−N(4)	1.946(4)
Co(1)−N(3)	2.028(4)	Co(1)−N(1)	2.040(4)
S(1)−O(2)	1.449(3)	S(1)−O(1)	1.452(3)
S(1)−N(2)	1.577(4)	S(1)−C(7)	1.768(5)
S(2)−O(3)	1.437(3)	S(2)−O(4)	1.446(3)
S(2)−N(4)	1.586(4)	S(2)−C(20)	1.772(5)
N(1)−C(5)	1.335(6)	N(1)−C(1)	1.352(6)
N(2)−C(6)	1.476(5)	N(3)−C(18)	1.355(6)
N(3)−C(14)	1.355(6)	N(4)−C(19)	1.459(5)
C(1)−C(2)	1.372(7)	C(2)−C(3)	1.353(8)
C(3)−C(4)	1.377(7)	C(4)−C(5)	1.386(6)
C(5)−C(6)	1.497(6)	C(7)−C(12)	1.376(6)
C(7)−C(8)	1.382(6)	C(8)−C(9)	1.379(7)
N(2)−Co(1)−N(4)	134.84(17)	N(2)−Co(1)−N(3)	123.64(16)
N(4)−Co(1)−N(3)	81.37(16)	N(2)−Co(1)−N(1)	82.08(16)
N(4)−Co(1)−N(1)	117.84(16)	N(3)−Co(1)−N(1)	122.65(16)
O(2)−S(1)−O(1)	117.6(2)	O(2)−S(1)−N(2)	105.4(2)
O(1)−S(1)−N(2)	113.1(2)	O(2)−S(1)−C(7)	106.1(2)
O(1)−S(1)−C(7)	106.6(2)	N(2)−S(1)−C(7)	107.5(2)
O(3)−S(2)−O(4)	118.1(2)	O(3)−S(2)−N(4)	107.0(2)
O(4)−S(2)−N(4)	111.5(2)		

Molecular Structure of $[Co^{III}L_2L^o]$ (3)

The molecular structure of $[Co^{III}L_2L^o]$ is shown in Figure 3, together with the adopted atomic numbering scheme. The main bond lengths and angles are given in Table 4. The structure consists of monomer $[Co^{III}L_2L^o]$ units. The cobalt atom is in a $[CoN_6]$ environment produced by two amide and two pyridine nitrogen atoms of two bidentate monoanionic tosylamide ligands and two nitrogen atoms of the ligand L^o, formed by the trimerisation of three molecules of the acetonitrile used as the solvent in the electrochemical cell. Both amide nitrogen atoms are in a *trans* disposition.

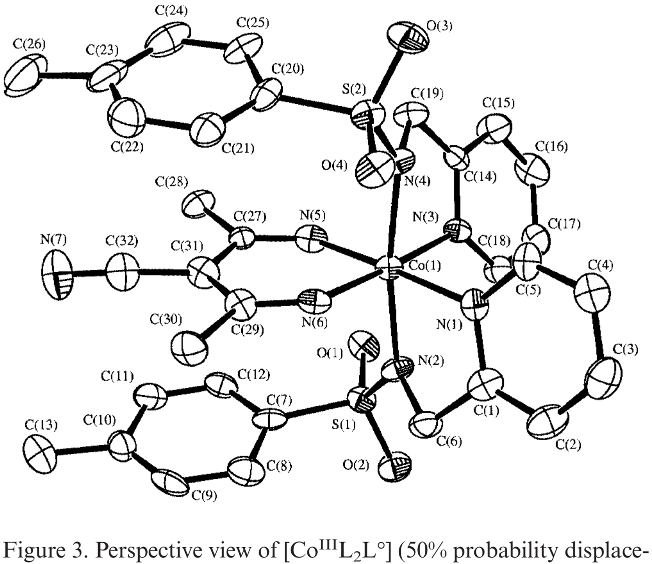


Figure 3. Perspective view of $[Co^{III}L_2L^o]$ (50% probability displacement ellipsoids)

Table 4. Selected bond lengths [Å] and angles [°] for the complex $[Co^{III}L_2L^o]$

Co(1)−N(6)	1.891(6)	Co(1)−N(5)	1.892(7)
Co(1)−N(3)	1.950(6)	Co(1)−N(4)	1.959(5)
Co(1)−N(2)	1.960(5)	Co(1)−N(1)	1.965(6)
S(1)−O(1)	1.422(5)	S(1)−O(2)	1.440(5)
S(2)−O(3)	1.433(5)	S(2)−O(4)	1.444(5)
S(1)−N(2)	1.591(5)	S(2)−N(4)	1.588(5)
S(1)−C(7)	1.775(9)	S(2)−C(20)	1.765(8)
N(1)−C(1)	1.368(9)	N(1)−C(5)	1.331(8)
N(2)−C(6)	1.458(8)	N(3)−C(14)	1.350(9)
N(3)−C(18)	1.321(8)	N(4)−C(19)	1.472(8)
N(5)−C(27)	1.275(10)	N(6)−C(29)	1.276(9)
N(7)−C(32)	1.155(6)	C(27)−C(28)	1.498(10)
C(29)−C(30)	1.552(10)	C(29)−C(31)	1.386(11)
N(6)−Co(1)−N(5)	88.8(3)	N(6)−Co(1)−N(3)	177.1(3)
N(5)−Co(1)−N(3)	89.2(3)	N(6)−Co(1)−N(4)	97.1(2)
N(5)−Co(1)−N(4)	89.7(3)	N(3)−Co(1)−N(4)	80.8(2)
N(6)−Co(1)−N(2)	90.2(2)	N(5)−Co(1)−N(2)	96.4(3)
N(3)−Co(1)−N(2)	92.1(2)	N(4)−Co(1)−N(2)	170.59(19)
N(6)−Co(1)−N(1)	90.6(2)	N(5)−Co(1)−N(1)	177.4(3)
N(3)−Co(1)−N(1)	91.5(18)	N(4)−Co(1)−N(1)	92.9(2)
N(2)−Co(1)−N(1)	81.0(2)		

The $Co-N_{amide}$ and $Co-N_{py}$ bond lengths have similar values. The average $Co-N_{py}$ bond length (1.957(5) Å) is longer than those found in other octahedral cobalt(III) complexes with pyridine nitrogen donor ligands, such as 1.882(5) Å in $[Co^{III}L^1]^+$ {HL^1 = 3,11-bis(methoxycarbonyl)-7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}[14] and 1.884(3) Å in $[Co^{III}L^3]$ [HL^3 = 3,7,11-tris(carboxymethyl)-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene][14] or 1.911(3) and 1.915(3) Å in $[Co^{III}(dpkH)_2](MeO)(MeOH)$ [dpkh = bis(2-pyridyl) ketone hydrate],[15] but is only slightly longer than 1.934(2) Å found in the complex $[Co^{III}L(OH)](ClO_4)_2$ [L = 2,6-bis(1′,3′-diamino-2′-methylprop-2′-yl)pyridine].[16] The $Co-N_{amide}$ bond length, with an average value of 1.959(5) Å, is similar to those found in other cobalt(III) amide complexes, such as 1.97(2) Å in $[Co(2\text{-amino-4-imino-2-methylpentane})_2(\text{methazolamidate})(NH_3)](NO_3)_2$.[17]

Bond lengths and angles within the framework of the pyridinesulfonamide ligand fall within the range found for other related metal complexes with similar ligands.[9,18]

The Co−N bond lengths from the ligand L^o are equal [Co−N(5) = 1.892(7) and Co−N(6) = 1.891(6) Å] and similar to those found in other hexacoordinated cobalt complexes with ligands possessing the same chemical skeleton: 1.995(5) Å in [Co(*R*-ala)-(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)-$Br_2\cdot 3H_2O$[19] or 2.009(5) Å in *cis*-$[Co^{III}L^2Cl_2]Cl$, in which L^2 stands for (5*RS*,7*SR*)-dimethyl-1,4,8,11-tetraazacyclooctatetradecane.[20] The bond angles have normal values for a six-membered chelate ring and are 88.8°. The bond lengths N−C and C−C in the new ligand L^o are essentially identical to those found in the other complexes with this ligand.[11,12] The N(5)−C(27) [1.275(10) Å] and N(6)−C(29) [1.276(9) Å] bond lengths are in agreement with the value of 1.30 Å proposed for a C=N double bond,[21] and the C(32)−N(7) bond length of 1.155(6) Å is shorter than for C=N but not as short as for a C≡N triple bond.[22] The C−C bonds in the chelate ring and the C(31)−C(32) bond are shorter [1.386(11)−1.432(11) Å] than the other C−C bonds [1.498(10)−1.522(10) Å]. The C(31)−C(32)−N(7) angle is very close to the theoretical value for a linear disposition [176.9(5)°].

The crystal packing is such that the molecules and the Co−C(9)−C(8)−N(7) units of adjacent complex molecules appear to form chains parallel to the *b* axis. The distance from the N(7) atom of a given molecule to the Co atom of the neighbouring molecule is 4.615(5) Å.

Spectroscopic Studies

The IR spectra of the complexes are in accordance with the X-ray data discussed above. The ligand HL shows a broad band at around 3095 cm^{-1}, attributable to ν(N−H). This band is absent in the IR spectra of the complexes, a fact in agreement with the deprotonation of the N−H amide bond during the electrosynthesis. The stretching band of the pyridine ring, observed between 1600 and 1400 cm^{-1} and the ring deformation bands, which appear at about 600 and 400 cm^{-1}, are shifted to higher frequencies in the complexes. This behaviour has been proposed as evidence for the coordination of the pyridine nitrogen atom to the metal ion,[23] as confirmed by the structural data. In addition, the spectrum of the $[Co^{III}L_2L^o]$ complex also shows a sharp band at 3350 cm^{-1}, assigned to ν(N−H), as well as another band at 2190 cm^{-1} due to ν(C≡N) of the new ligand L^o.

The IR spectra of the mixed complexes containing 2,2′-bipyridine or 1,10-phenanthroline as additional ligands show the bands characteristic of these coordinated ligands[24,25] (bipy: ca. 770 and 720 cm^{-1}; phen: ca. 1520, 847 and 722 cm^{-1}).

The diffuse reflectance spectrum of $[Co^{II}L_2]$ in the NIR/Vis region shows two multicomponent bands, one at 7600, 8900 and 11200 cm^{-1} [assigned to $^4A_2 \rightarrow {}^4T_1(F)$ (ν_2)] and the other at 17100, 19455 and 20790 cm^{-1} [due to $^4A_2 \rightarrow {}^4T_1(F)$ (ν_3)], both of which are consistent with a distorted tetrahedral environment for the metal ion.[26] The $^4A_2 \rightarrow {}^4T_1$ (P) (ν_1) transition was not observed, but its position at ca. 5300 cm^{-1} was calculated by the method described by Lever. The presence of three closely spaced transitions in the spectrum of $[Co^{II}L_2]$ arises due to distortion from the regular tetrahedral symmetry, a situation resulting from the inequivalence of the pyridyl and sulfonamide donor atoms and the restrictive bite angle of the chelating ligands. At room temperature this complex has a magnetic moment of 4.0 B.M., which is well within the range expected for tetrahedral cobalt(II) compounds.

The solid-state electronic spectra of the mixed complexes $[Co^{II}L_2L']$ between 20000 and 5000 cm^{-1} are all very similar, but differ from those found for the $[Co^{II}L_2]$ and $[Co^{III}L_2L^o]$ complexes. The former complexes gave rise to three bands in the regions 7400−9500, 14600−15150 and 21800−23000 cm^{-1}, assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) and $^3T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_3)$ transitions, respectively, in a distorted octahedral field.[26] The magnetic moments of these complexes at room temperature are in the range 4.60−4.80 B.M., and these values are on the low side of the range expected for octahedral cobalt(II) complexes, probably as a result of a reduced orbital contribution. The magnetic moment of the $[Co^{III}L_2L^o]$ complex shows that this compound is diamagnetic and which is consistent with a low-spin d^6 octahedral complex. The solid-state electronic spectrum shows two bands at 15200 and 21800 cm^{-1}, as would be expected for low-spin six-coordinated cobalt(III) complexes. The first band has been attributed to a $^1A_{1g} \rightarrow {}^1T_{1g}$ transition and the other band to a $^1A_{1g} \rightarrow {}^1T_{2g}$ transition.[26]

In the FAB mass spectra of $[Co^{II}L_2]$, $[Co^{III}L_2L^o]$, $[Co^{II}L_2bipy]$ and $[Co^{II}L_2phen]$, the molecular ion peaks are observed at *m*/*z* = 582, 703, 737 and 762, respectively, together with corresponding peaks at *m*/*z* = 426, 442, 476 and 500 formed by loss of one tosyl ligand from each complex. A peak is also observed at *m*/*z* = 580 in the spectrum of $[Co^{III}L_2L^o]$, and this corresponds to a fragment formed by loss of the ligand L^o.

Experimental Section

Materials and Instrumentation: Cobalt (Aldrich Chemie) was used as plates (ca. 2 × 2 cm). All other reagents, including 1,10-phenanthroline and 2,2′-bipyridine, were used as supplied. The C,H,N,S analyses of the compounds were performed with a Carlo−Erba EA 1108 microanalyzer. IR spectra were recorded as KBr mulls with a Bruker IFS-66V spectrophotometer. The ^1H NMR spectrum of the ligand was recorded with a Bruker AMX 300 MHz spectrometer, with $[D_6]DMSO$ as solvent. The chemical shifts were recorded against TMS as an internal standard. FAB mass spectra were recorded with an Autospec-Micromass instrument, with 3-nitrobenzyl alcohol (3-NBA) as the matrix. Solid-state electronic spectra were recorded with a Shimadzu UV 3101 PC apparatus. Magnetic measurements were obtained with a DMS VSM 1160 instrument.

Synthesis of the Ligand HL (1): The ligand HL was prepared from equimolar amounts of 2-aminomethylpyridine (1.00 mL, 10.1 mmol) and tosyl chloride (1.93 g, 10.1 mmol) in dichloromethane (40 mL). Aqueous NaOH (10%) was added to the mixture until pH = 8 was reached, and a white product was obtained.[27] The solid was filtered off and dried in vacuo. Yield 78%. The purity of the product was assessed by microanalysis, IR and ^1H NMR spectroscopy. Crystals suitable for X-ray structure determination were obtained by crystallisation from dichloromethane. IR (KBr): $\tilde{\nu}$ = 3094 [ν(N−H)], 1598−1385 $[\nu(C{=}C, C{=}N)_{py}]$, 1328 $[\nu_{as}(SO_2)]$, 1164 $[\nu_s(SO_2)]$ cm^{-1}. ^1H NMR ($[D_6]DMSO$): δ = 11.6 (s, 1 H, $N{-}H_{tosyl}$), 8.5 (d, 1 H, $2\text{-}H_{py}$), 2.1 (s, 3 H, Me_{tosyl}) ppm. $C_{13}H_{15}N_2O_{2.5}S$ (271.3): calcd. H 5.58, C 57.55, N 10.33, S 11.79; found H 5.38, C 57.52, N 10.10, S 12.22.

Preparation of the Complexes (General Procedure): The complexes were formed by an electrochemical procedure.[28] This method allows the preparation of different products simply by changing the conditions of the electrochemical reaction. The cell consisted of two electrodes submerged in a solution of the tosylated ligand and a small amount of tetraethylammonium perchlorate (ca. 15−20 mg) as a current carrier in acetonitrile. The cathode was a platinum wire and the anode a plate of the appropriate metal. For the synthesis of mixed complexes, the corresponding coligand − 1,10-phenanthroline or 2,2′-bipyridine − was also added to the solution. Applied voltages of 9−15 V allowed sufficient current flow for smooth dissolution of the metal. In all cases the electrochemical synthesis was carried out at room temperature. The cell can be summarised as $Pt(-)/CH_3CN + HL/M(+)$.

Preparation of $[Co^{II}L_2]$ (2): Electrolysis of an acetonitrile solution containing HL (0.2932 g, 1.12 mmol) and a small amount of tetraethylammonium perchlorate (ca. 25 mg) at 10 mA and 9 V for 3 h dissolved 32 mg of cobalt (E_f = 0.49 mol·F^{-1}). At the end of the experiment, a purple solution had been obtained and was allowed to stand for a few days. Purple crystals suitable for X-ray diffraction formed, and these were collected and dried in vacuo. The compound was characterised as $[Co^{II}L_2]$. IR (KBr): $\tilde{\nu}$ = 1611−1439 $[\nu(C{=}C, C{=}N)_{py}]$, 1275 $[\nu_{as}(SO_2)]$, 1147 $[\nu_s(SO_2)]$ cm^{-1}. $C_{26}H_{26}CoN_4O_4S_2$ (581.5): calcd. H 4.51, C, 53.70, N 9.63, S 11.01; found H 4.47, C 53.52, N 9.62, S 9.76.

Preparation of $[Co^{III}L_2L^o]$ (3): Electrolysis of an acetonitrile solution containing HL (0.1947 g, 0.7432 mmol) and a small amount of tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 20.8 V for 2 h dissolved 20 mg of cobalt (E_f = 0.46 mol·F^{-1}). At the end of the experiment a brown solution had formed, with brown crystals at the bottom of the vessel. These crystals were filtered off and dried in vacuo and were suitable for X-ray crystallography. The compound was characterised as $[Co^{III}L_2L^o]$. IR (KBr): $\tilde{\nu}$ = 3354 [ν(NH)], 2189 [ν(C≡N)], 1604−1396 $[\nu(C{=}C, C{=}N)_{py}]$, 1280 $[\nu_{as}(SO_2)]$, 1134 $[\nu_s(SO_2)]$ cm^{-1}. $C_{32}H_{34}CoN_7O_4S_2$ (703.7): calcd. H 4.87, C 54.62, N 13.93, S 9.09; found H 4.88, C 54.45, N 13.41, S 9.75.

Preparation of $[Co^{II}L_2(bipy)]$ (4): Electrolysis of an acetonitrile solution containing HL (0.1947 g, 0.7432 mmol), 2,2′-bipyridine (0.0584 g, 0.3715 mmol) and a small amount of tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 20.3 V for 2 h dissolved 22 mg of cobalt (E_f = 0.51 mol·F^{-1}). At the end of the experiment a brown solid had formed, and this was filtered off, washed with acetonitrile and dried in vacuo. The compound was characterised as $[Co^{II}L_2(bipy)]$. IR (KBr): $\tilde{\nu}$ = 1628−1492 $[\nu(C{=}C, C{=}N)_{py}]$, 1283 $[\nu_{as}(SO_2)]$, 1159 $[\nu_s(SO_2)]$ cm^{-1}. $C_{36}H_{34}CoN_6O_4S_2$ (737.7): calcd. H 4.61, C 58.60, N 11.39, S 8.68; found H 4.57, C 59.39, N 12.07, S 7.92.

Preparation of $[Co^{II}L_2(phen)]$ (5): Electrolysis of an acetonitrile solution containing HL (0.1947 g, 0.7432 mmol) and a small amount of tetraethylammonium perchlorate (ca. 20 mg) at 10 mA and 24.6 V for 2 h dissolved 23 mg of cobalt (E_f = 0.53 mol·F^{-1}). At the end of the experiment a dark brown solid had formed, and this was filtered off, washed with acetonitrile and ether, and dried in vacuo. The compound was characterised as $[Co^{II}L_2(phen)]$. IR (KBr): $\tilde{\nu}$ = 1628−1429 $[\nu(C{=}C, C{=}N)_{py}]$, 1281 $[\nu_{as}(SO_2)]$, 1160 $[\nu_s(SO_2)]$ cm^{-1}. $C_{38}H_{34}CoN_6O_4S_2$ (761.8): calcd. H 4.46, C 59.90, N 11.03, S 8.40; found H 4.79, C 59.37, N 11.00, S 8.28.

Crystal Structure Determination: Crystals of HL (**1**) and $[Co^{III}L_2L^o]$ (**3**) were mounted on glass fibres and used for data collection with an Enraf Nonius CAD4 diffractometer, while a Siemens SMART CCD area detector diffractometer was used in the case of $[Co^{II}L_2]$ (**2**). Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator) was used for the collection of the intensity data by a 2θ/ω-scan technique. Decomposition of the crystals did not occur during data collection. Corrections were applied for Lorentz and polarisation effects and for absorption.[29] The structures were solved by direct methods; missing atoms were located in the difference Fourier maps and included in subsequent refinement cycles. The structures were refined by full-matrix, least-squares refinement on F^2, with anisotropic displacement parameters used for all non-

Table 5. Summary of crystal data and structure refinement

	HL	$[Co^{II}L_2]$	$[Co^{III}L_2L^o]$
Empirical formula	$C_{13}H_{15}N_2O_{2.50}S$	$C_{26}H_{26}CoN_4O_4S_2$	$C_{32}H_{34}CoN_7O_4S_2$
Formula mass	271.33	581.56	703.71
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, *C*2/*c*	monoclinic, $P2_1/n$	orthorhombic, *Pca*2(1)
a [Å]	27.145(11)	13.0552(3)	16.310(4)
b [Å]	6.0119(12)	7.8373(2)	10.4858(15)
c [Å]	16.690(7)	26.2839(2)	17.931(4)
β [°]	99.10(2)	95.1350(10)	90.00
Volume [Å^3]	2689(2)	2678.51(9)	3066.6(11)
Z	8	4	4
Density (calculated) [Mg/m^3]	1.340	1.442	1.524
Absorption coefficient [mm^{-1}]	0.241	0.836	0.747
F(000)	1144	1204	1464
Crystal size [mm], colour	0.35 × 0.15 × 0.10, colourless	0.15 × 0.10 × 0.05, purple	0.30 × 0.25 × 0.15, caramel
θ range for data collection [°]	3.04−30.01	1.56−28.27	1.94−24.97
Index ranges	$-37 \le h \le 37$, $0 \le k \le 8$, $0 \le l \le 22$	$-17 \le h \le 17$, $-10 \le k \le 5$, $-35 \le l \le 33$	$0 \le h \le 19$, $0 \le k \le 12$, $-21 \le l \le 21$
Reflections collected	4039	18454	2915
Independent reflections	3908 [R_{int} = 0.0384]	6573 [R_{int} = 0.1040]	2909 [R_{int} = 0.0159]
Reflections observed	1304	2752	2210
Criterion for observation	$> 2\sigma(I)$	$> 2\sigma(I)$	$> 2\sigma(I)$
Data/restraints/parameters	3908/0/218	6573/0/336	2909/1/427
Goodness-of-fit on F^2	1.027	1.046	1.039
Final *R* indices [$I > 2\sigma(I)$]	0.0840/0.1750	0.0780/0.1074	0.0401/0.0714
Absolute structure parameter			0.00(3)
Largest diff. peak and hole [e·Å^{-3}]	0.297 and −0.293	0.360 and −0.436	0.384 and −0.274

hydrogen atoms except those of the methyl group [C(20)] of the ligand HL, which were located in their calculated positions (C−H 0.96 Å). In all cases, hydrogen atoms were included by using a riding model with C−H distances of 0.93−0.97 Å and fixed isotropic thermal parameters. The weighting scheme of the form $\omega = 1/\sigma^2(F)$ was introduced, and the refinement proceeded smoothly to convergence with a maximum delta/σ of 0.001. The absolute configuration was determined for **3**.[30] The crystallographic programs used for the structure solutions and refinement were from SHELX97.[31] Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography.[32] The crystal data and summary of data collection and structure refinement for these compounds are given in Table 5. Selected bond lengths and angles for **1**, **2** and **3** are given in Tables 1, 3 and 4. ORTEP3[33] drawings of the molecules with the numbering schemes used are shown in Figures 1−3. CCDC-171729 (**1**), -171730 (**2**) and -171731 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] L. Antolini, L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigliano, L. Menablue, G. C. Pellacani, *J. Am. Chem. Soc.* **1985**, *107*, 1369−1375.

[2] H. Siegel, R. B. Martin, *Chem. Rev.* **1982**, *82*, 385−426.

[3] C. A. Otter, S. M. Couchman, J. C. Jeffery, K. L. V. Mann, E. Psillakis, M. D. Ward, *Inorg. Chim. Acta* **1998**, *278*, 178−184.

[4] M. L. Durán, J. A. García-Vázquez, J. Romero, A. Castiñeiras, A. Sousa, A. D. Garnovskii, D. A. Garnovskii, *Polyhedron* **1997**, *16*, 1707−1711.

[5] E. Eliopoulos, B. Sheldrick, S. Hamodrakas, *Acta Crystallogr., Sect. C* **1983**, *39*, 1693−1695.

[6] A. K. Basak, S. Chaudhuri, S. K. Mazumdar, *Acta Crystallogr., Sect. C* **1984**, *40*, 1848−1851.

[7] I. Bar, J. Bernstein, *J. Pharm. Sci.* **1985**, *74*, 255−263 and references therein.

[8] J. Bernstein, *Acta Crystallogr., Sect. C* **1988**, *44*, 900−902.

[9] S. Cabaleiro, J. Castro, E. Vázquez-López, J. A. García-Vázquez, J. Romero, A. Sousa, *Polyhedron* **1999**, *18*, 1669−1674.

[10] T. S. Cameron, K. Prout, B. Denton, R. Spagna, E. White, *J. Chem. Soc., Perkin Trans. 2* **1975**, 176−185.

[11] M. R. Kopp, T. Krauter, A. Dashti-Mommertz, B. Neumuller, *Organometallics* **1998**, *17*, 4226−4231.

[12] M. R. Kopp, B. Neumuller, *Z. Anorg. Allg. Chem.* **1999**, *625*, 739−745; *Z. Anorg. Allg. Chem* 1246−1248.

[13] J. A. García-Vázquez, J. Romero, M. L. Durán, A. Sousa, A. D. Garnovskii, A. S. Burlov, D. A. Garnovskii, *Polyhedron* **1998**, *17*, 1547−1552.

[14] J. Costa, R. Delgado, M. G. B. Drew, V. Félix, R. T. Henriques, J. C. Waerenborgh, *J. Chem. Soc., Dalton Trans.* **1999**, 3253−3265.

[15] C. Hemmert, M. Renz, H. Gornitzka, S. Soulet, B. Meunier, *Chem. Eur. J.* **1999**, 1766−1774.

[16] T. Poth, H. Paulus, H. Elias, R. van Eldik, A. Grohmann, *Eur. J. Inorg. Chem.* **1999**, 643−650.

[17] G. Alzuet, S. Ferrer, J. Casanova, J. Borras, A. Castiñeiras, *Inorg. Chim. Acta* **1993**, *203*, 79−84.

[18] S. Cabaleiro, J. Castro, J. A. García-Vázquez, J. Romero, A. Sousa, *Polyhedron* **2000**, *19*, 1607−1614.

[19] M. Yashiro, M. Ajioka, S. Yano, K. Toriumi, T. Ito, S. Yoshikawa, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2255−2261.

[20] K. Mochizuki, K. Ikeuchi, T. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2629−2634.

[21] J. N. Brown, R. L. Towns, L. M. Trefonas, *J. Am. Chem. Soc.* **1970**, *92*, 7436−7440.

[22] V. Chebolu, R. R. Whittle, A. Sen, *Inorg. Chem.* **1985**, *24*, 3082−3085, and references therein.

[23] A. Castiñeiras, J. A. Castro, M. L. Durán, J. A. García-Vázquez, A. Macías, J. Romero, A. Sousa, *Polyhedron* **1989**, *21*, 2543−2549 and references therein.

[24] R. G. Inskeep, *J. Inorg. Nucl. Chem.* **1962**, *24*, 763−776.

[25] A. A. Schilt, R. C. Taylor, *J. Inorg. Nucl. Chem.* **1959**, *9*, 211−211.

[26] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, **1984**.

[27] *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., Longman Scientific & Technical, New York, **1989**, p. 879.

[28] J. J. Habeeb, D. G. Tuck, F. H. Walters, *J. Coord. Chem.* **1978**, *8*, 27−32.

[29] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158−166.

[30] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876−881.

[31] G. M. Sheldrick, *SHELX97* (includes SHELXS-97, SHELXL-97, CIFTAB) − *Programs for Crystal Structure Analysis* (Release 97-2), Institut für Anorganische Chemie der Universität, Tammanstrasse 4, 3400 Göttingen, Germany, **1998**.

[32] *International Tables for Crystallography* (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1995**, vol. C.

[33] ORTEP3 for Windows: L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

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