

Flexidentate Behaviour of 2-Pyridylsulfonamides – Direct Electrochemical Synthesis and Spectroscopic and X-ray Characterisation of Neutral Copper(II) Complexes of *N*-(2-Pyridyl)sulfonamides

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Dedicated to the memory of Professor D. G. Tuck

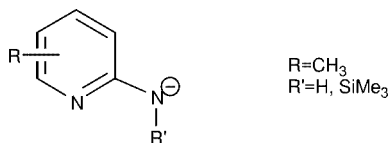
Keywords: Copper / S ligands / Electrochemical synthesis / N ligands

Copper complexes with potentially bidentate *N*-(2-pyridyl)-sulfonamide ligands have been synthesised by the electrochemical oxidation of the metal in an acetonitrile solution of the neutral amide and additional bidentate N–N coligands. The compounds have been characterised by microanalysis and EPR, vibrational and electronic spectroscopy. In repres-

entative cases the structures were also determined by X-ray diffraction methods. Various coordination behaviour is found for the ligands, which act in a *N,N'*-bidentate or *N,O*-bidentate manner, the latter giving abnormally short Cu–O bonds. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

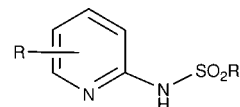
Metal complexes containing amide ligands are of great recent interest^[1–4] because they are easily made, and the substituents can be readily amended so as to tune their bite angle and steric hindrance. The chemistry of metal complexes containing pyridine-functionalised amido ligands of the type shown in Scheme 1 has received much attention.^[5–9] The bulky substituents on these ligands stabilise the metal complexes.



Scheme 1

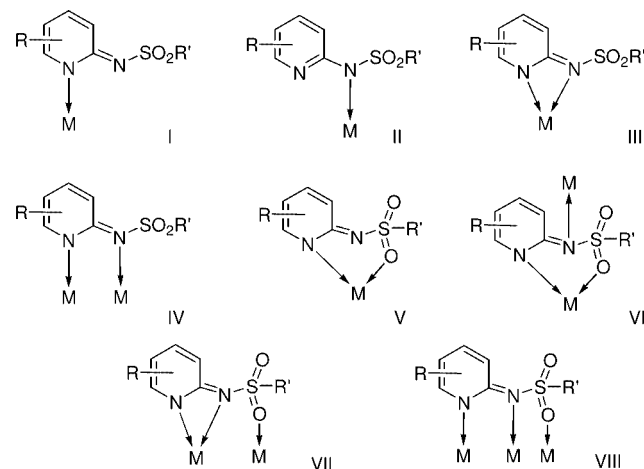
Consequently, it was decided to study the chemistry of the metal complexes of sulfonyl-2-pyridine-amines. These li-

gands, Scheme 2, contain a bulky sulfonyl group as a substituent of the exocyclic nitrogen atom. In addition, its electron-withdrawing effect increases the acid character of the NH group and makes ligand deprotonation easier.^[4]



Scheme 2

These ligands can coordinate to the metal in several different ways (Scheme 3).



Scheme 3

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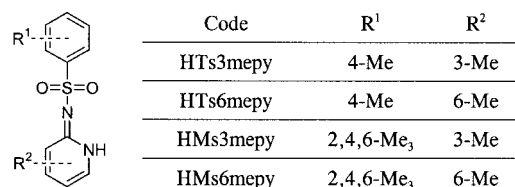
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Coordination modes I and II have been found in zinc compounds. For complexes showing coordination mode I, a weak interaction between the metal and the exocyclic nitrogen atom is present,^[10] while mode II exhibits a weak interaction between the zinc and the pyridine nitrogen atom.^[11] Coordination mode III is the most common, and has been found in cobalt(II),^[12] nickel(II),^[13] and cadmium(II)^[14,15] complexes. Coordination mode IV has only been found in copper(II)^[9] and silver(I)^[9,16] complexes, and coordination mode V has only been found in zinc(II)^[11] and cadmium(II)^[15] complexes. Coordination modes VI and VII have been found in a polymer compound of cadmium(II)^[14] and the coordination mode VIII only occurs in silver(I) complexes.^[16]

Coordination mode IV appears to have only been found with copper(II) and silver(I). When the ligand has no substituent on the pyridine ring ($R = H$) the compound is dinuclear.^[9] To check if the nuclearity and the coordination mode could be modified, we introduced a methyl group at position 3 or 6 on the pyridine ring to determine the influence of the steric hindrance produced by such substitution on the coordination of the pyridine and the sulfonamide nitrogen atoms. Substitution at position 4 does not influence the coordination mode and a dinuclear compound is again obtained.^[16] Therefore, and to continue similar studies on Zn^{II} ^[11] and Cd^{II} ,^[15] we report here the electrochemical synthesis and characterisation of several heteroleptic copper(II) complexes with a number of benzenesulfonyl-2-pyridineamide ligands. The pyridine ring contains one methyl group and the benzene ring also contains one methyl group (*p*-toluene group) or, alternatively, three methyl groups (mesitylene group) (Scheme 4).



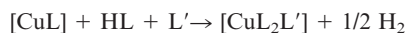
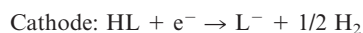
Scheme 4. The sulfonamide ligands

Results and Discussion

Anodic oxidation of copper metal in a non-aqueous solution containing a weakly acidic ligand alone or as a mixture with a coligand, such as 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen), yields the products $[CuL_2H_2O]$ or $[CuL_2L']$, respectively, where L is the deprotonated form of the parent ligand and L' the coligand (i.e. bipy or phen) (see Exp. Sect.). The compounds are obtained by air concentration of the resulting solution as green air-stable crystalline products. They are insoluble in water and in most common organic solvents.

The electrochemical efficiency, defined as the amount of metal dissolved per number of Faradays, was close to 1.0 mol·F⁻¹ in all cases. This fact, along with the evolution of hydrogen at the cathode, is compatible with a reaction

mechanism involving the anodic oxidation to copper(I) and the deprotonation of the ligand at the cathode.



The oxidation of copper(I) by another HL molecule has been observed in other electrochemical processes involving copper anodes.^[17]

Description of the Structures

The crystal and molecular structures of several complexes and the ligand HMs3mepy have been determined by single crystal XRD. The crystal data are collected in Tables 12 and 13.

Structure of HMs3mepy

HMs3mepy crystallizes in the monoclinic $C2/c$ space group, $Z = 4$, and consists of molecules of [(2,4,6-trimethylphenyl)sulfonyl]imino-1*H*-3-methyl-2-pyridine associated two-by-two by intermolecular hydrogen bonds established between the pyridine nitrogen atom of one molecule and two sulfonamide oxygen atoms, one of which forms an intramolecular contact while the other is involved in an intermolecular contact with a neighbouring molecule. The imine nitrogen is not implicated in these bonds. This arrangement contrasts with the hydrogen network found in HTspy^[13] and HTs6mepy,^[15] where the hydrogen bonds involve the N_{py} and the $N_{sulfonamide}$ atoms. The methyl group in position 3 of the pyridine ring precludes the use of the $N_{sulfonamide}$ atom with HTs3mepy for steric reasons. This explanation is supported by the observed ligational mode of HTs3mepy (vide infra).

The structure of HTs3mepy and the atomic numbering scheme (Figure 1), and selected bond lengths and angles and hydrogen bond parameters (Table 1 and Table 2), are given here.

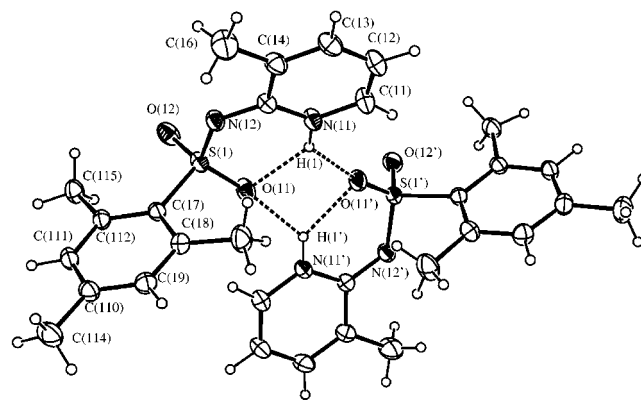


Figure 1. Structure of HMs3mepy

The bond lengths and bond angles are similar to those in other *N*-2-pyridinyl benzenesulfonamide derivatives.^[11,13,15] The hydrogen atom on the *N*-pyridine ring shows that the free ligand is the imido tautomer (I) rather than the amido

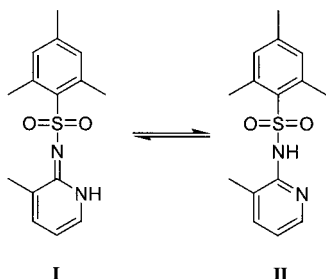
Table 1. Selected bond lengths [Å] and angles [°] for HMs3mepy

S–O(12)	1.4345(14)	S–O(11)	1.4517(12)
S–N(12)	1.5937(14)	S–C(17)	1.7821(16)
N(11)–C(15)	1.359(2)	N(11)–C(11)	1.364(2)
N(11)–H(1)	0.945(19)	N(12)–C(15)	1.326(2)
O(12)–S–O(11)	114.30(9)	O(12)–S–N(12)	108.89(8)
O(11)–S–N(12)	113.04(7)	O(12)–S–C(17)	109.76(8)
O(11)–S–C(17)	107.47(8)	N(12)–S–C(17)	102.71(7)

Table 2. Hydrogen bonds and short contacts for HMs3mepy (i: symmetry transformations used to generate equivalent atoms: $-x, y, 0.5 - z$)

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
N(11)–H(1)...O(11)	0.945(19)	2.00(2)	2.7209(18)	131.6(16)
N(11)–H(1)...O(11) ⁱ	0.945(19)	2.124(19)	2.8858(19)	136.7(16)
C(113)–H(11A)...N(12)	0.96	2.61	3.102(3)	112.2
C(113)–H(11B)...O(11)	0.96	2.47	3.086(3)	121.8
C(115)–H(11E)...O(12)	0.96	2.40	2.747(2)	100.9

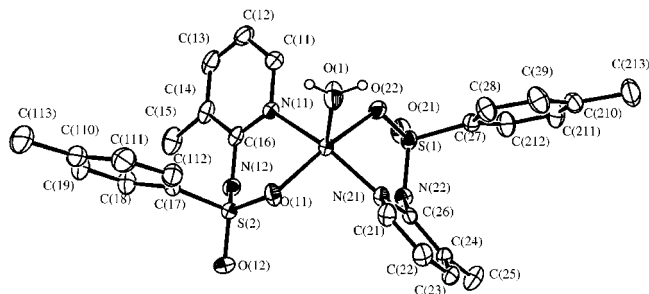
tautomer (II). This situation is similar to that described for related compounds (Scheme 5).^[11,13,15]



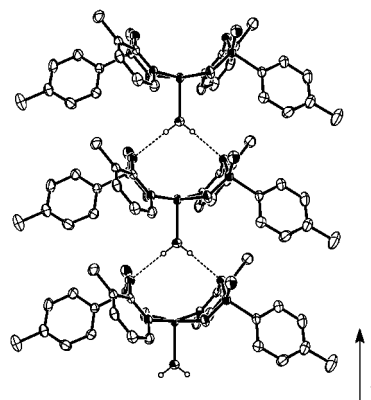
Scheme 5

Structure of [Cu(Ts3mepy)₂H₂O]

This compound crystallizes in the monoclinic $P2_1/c$ space group, $Z = 4$. Its structure is shown in Figure 2 together with the atomic numbering scheme.

Figure 2. Molecular structure of [Cu(Ts3mepy)₂H₂O]

The crystal structure can be described as discrete molecules of [Cu(Ts3mepy)₂H₂O] associated by intermolecular interactions. The hydrogen atoms of the coordinated water molecule are involved in hydrogen bonds with the amide nitrogen atoms that are not coordinated to the metal in such a way that infinite chains are formed parallel to the *b* axis (Figure 3). Selected bond lengths and angles are given in Table 3 and Table 4.

Figure 3. Supramolecular structure of [Cu(Ts3mepy)₂H₂O]Table 3. Selected bond lengths [Å] and angles [°] for [Cu(Ts3mepy)₂(H₂O)]

Cu–N(21)	1.974(2)	Cu–N(11)	1.980(2)
Cu–O(11)	2.0018(18)	Cu–O(22)	2.0130(18)
Cu–O(1)	2.160(2)	S(1)–O(21)	1.428(2)
N(21)–Cu–N(11)	164.73(9)	N(21)–Cu–O(11)	88.69(8)
N(11)–Cu–O(11)	89.81(8)	N(21)–Cu–O(22)	88.86(8)
N(11)–Cu–O(22)	89.72(8)	O(11)–Cu–O(22)	168.98(8)
N(21)–Cu–O(1)	97.00(9)	N(11)–Cu–O(1)	98.27(10)
O(11)–Cu–O(1)	95.88(10)	O(22)–Cu–O(1)	95.08(10)

Table 4. Hydrogen bonds for [Cu(Ts3mepy)₂(H₂O)] (Å and °). (i: symmetry transformations used to generate equivalent atoms: $x, y - 1, z$)

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O(1)–H(1)...N(12) ⁱ	0.81(3)	2.11(3)	2.917(3)	175(3)
O(1)–H(2)...N(22) ⁱ	0.85(3)	2.14(3)	2.984(3)	179(3)

The copper atom is coordinated by a molecule of water and two monoanionic (*N,O*)-bidentate ligands through the nitrogen of the pyridine ring and one oxygen atom of a sulfonic group. The sulfonamide nitrogen atoms are 3.039(2) and 3.093(2) Å, respectively, away from the copper atom, and so they are not bonded. Consequently, the coordination around the metal can be described as [CuN₂O₃]. This is quite surprising as sulfonyl oxygen atoms are not good donors, and copper(II) complexes containing ligands bonded through the sulfonamide oxygen donors are scarce.^[18,19] The environment around the central atom is square pyramidal with a very small distortion towards a

trigonal bipyramidal geometry ($\tau = 0.07$).^[20] The apical position of the pyramid is occupied by the oxygen atom of the water molecule and the base consists of an (N_2O_2) arrangement in a *trans* disposition. This base is almost planar ($rms = 0.0353$). The copper atom is 0.2273(11) Å above the plane.

The Cu–N bond lengths are in the normal range found for Cu–N_{py} bonds.^[4,21] However, the Cu–O bonds [Cu–O_{water} = 2.160(2); Cu–O(11) = 2.0018(18) and Cu–O(22) = 2.0130(18) Å] are unusually short for such O-donor atoms.^[21,22] Firstly, the apical Cu–O_{water} in pentacoordinate copper complexes are normally much longer than the Cu–O bonds in the basal plane.^[23,24] In addition, the Cu–O_{sulfonamide} bond is the shortest found so far in sulfonamide copper complexes.

Structures of the Complexes [Cu(Ts3mepy)₂bipy], [Cu(Ts3mepy)₂phen], [Cu(Ms3mepy)₂bipy] and [Cu(Ms3mepy)₂phen]

Complexes [Cu(Ts3mepy)₂bipy] and [Cu(Ts3mepy)₂phen] crystallize in the triclinic $P\bar{1}$ space group, $Z = 2$. Complexes [Cu(Ms3mepy)₂bipy] and [Cu(Ms3mepy)₂phen] crystallize in the monoclinic $P2_1/c$ space group, $Z = 4$. The compounds consist of discrete molecules without relevant intermolecular interactions.

The molecular structures are shown in Figures 4–7, together with the atomic numbering schemes. Selected bond lengths and angles are given in Table 5.

In all the compounds, one of the sulfonamide ligands behaves in a (*N,O*)-bidentate manner and the other one is *N*-monodentate. The coligand (2,2-bipyridine or 1,10 phenanthroline) acts as an (*N,N'*)-bidentate ligand. The different

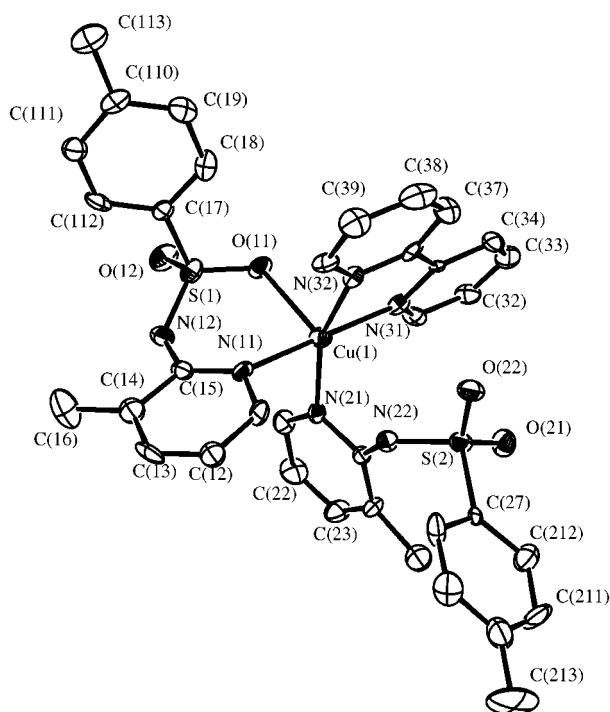


Figure 4. Molecular structure of [Cu(Ts3mepy)₂bipy]

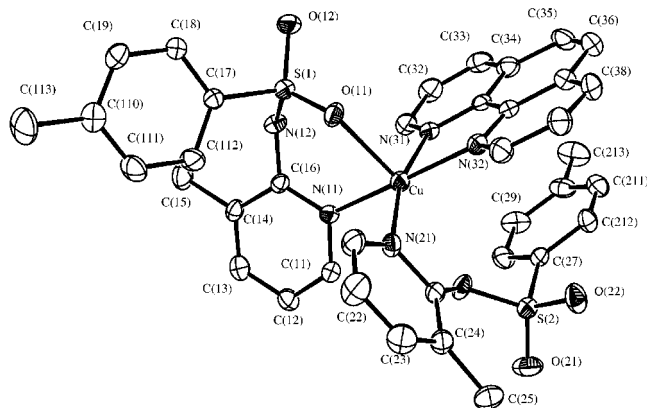


Figure 5. Molecular structure of [Cu(Ts3mepy)₂phen]

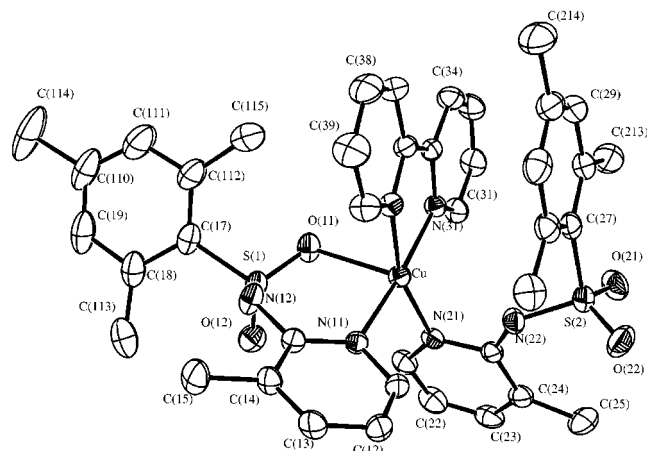


Figure 6. Molecular structure of [Cu(Ms3mepy)₂bipy]

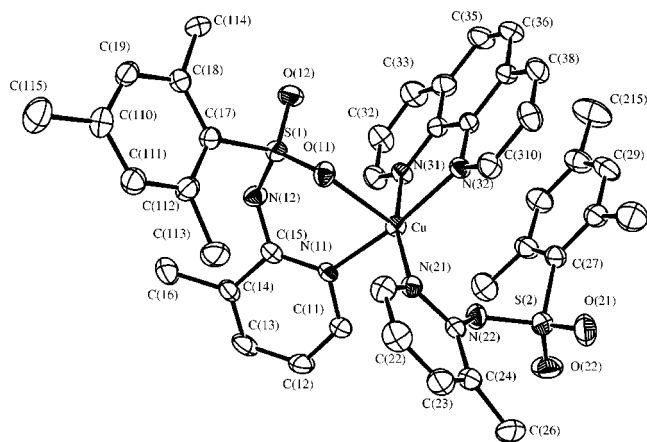


Figure 7. Molecular structure of [Cu(Ms3mepy)₂phen]

coordination behaviour of the two tosylamide ligands is the most significant feature of the structures.

The copper atom is in a pentacoordinate environment with four Cu–N bonds close to 2.0 Å, Cu–O bonds ranging from 2.209(6) to 2.291(2) Å and with another Cu–N_{sulfonamide} interaction, not considered as a bond, ranging from 2.592(7) Å for [Cu(Ts3mepy)₂bipy] to 2.726(3) Å for [Cu(Ms3mepy)₂phen] (Table 5).

The coordination polyhedron is best described as square pyramidal with a distortion towards a trigonal bipyramidal

Table 5. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for the pentacoordinate compounds $[\text{CuL}_2\text{L}']$, $\text{L}' = \text{bipy}$ or phen

	$[\text{Cu}(\text{Ts3mepy})_2\text{bipy}]$	$[\text{Cu}(\text{Ts3mepy})_2\text{phen}]$	$[\text{Cu}(\text{Ms3mepy})_2\text{bipy}]$	$[\text{Cu}(\text{Ms3mepy})_2\text{phen}]$
$\text{Cu}(1)-\text{O}(11)$	2.209(6)	2.244(3)	2.2914(18)	2.263(2)
$\text{Cu}(1)-\text{N}(11)$	2.019(8)	2.004(4)	2.0259(19)	2.032(3)
$\text{Cu}(1)-\text{N}(21)$	2.020(7)	2.003(4)	1.984(2)	1.994(3)
$\text{Cu}(1)-\text{N}(31)$	1.999(8)	2.039(4)	2.0355(19)	2.018(3)
$\text{Cu}(1)-\text{N}(32)$	2.023(8)	2.029(4)	2.005(2)	2.039(3)
$\text{Cu}(1)-\text{N}(22)$	2.592(7)	2.665(4)	2.620(2)	2.726(3)
$\text{N}(11)-\text{Cu}(1)-\text{N}(21)$	89.9(3)	92.77(14)	93.61(8)	94.01(12)
$\text{N}(11)-\text{Cu}(1)-\text{N}(32)$	96.0(3)	175.90(17)	93.86(8)	172.36(13)
$\text{N}(11)-\text{Cu}(1)-\text{N}(31)$	175.8(3)	94.91(15)	173.69(9)	93.93(12)
$\text{N}(11)-\text{Cu}(1)-\text{O}(11)$	90.4(3)	87.64(14)	92.59(7)	86.77(10)
$\text{N}(21)-\text{Cu}(1)-\text{N}(31)$	92.4(3)	165.11(17)	92.63(8)	164.93(12)
$\text{N}(21)-\text{Cu}(1)-\text{N}(32)$	158.8(3)	90.98(16)	163.31(9)	92.38(12)
$\text{N}(21)-\text{Cu}(1)-\text{O}(11)$	103.7(3)	92.07(16)	104.56(8)	93.38(11)
$\text{N}(31)-\text{Cu}(1)-\text{O}(11)$	92.4(3)	100.97(14)	84.91(7)	99.84(10)
$\text{N}(32)-\text{Cu}(1)-\text{O}(11)$	96.6(3)	93.88(14)	89.98(8)	88.69(10)
$\text{N}(31)-\text{Cu}(1)-\text{N}(32)$	80.6(3)	81.07(17)	80.36(8)	80.79(12)

Table 6. Environment around the metal

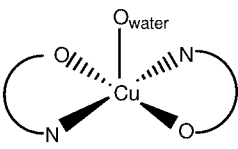
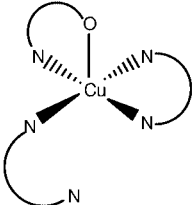
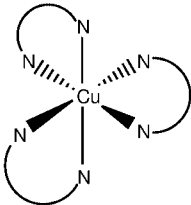
$[\text{Cu}(\text{Ts3mepy})_2(\text{H}_2\text{O})]$	$[\text{Cu}(\text{Ts3mepy})_2\text{bipy}]$ $[\text{Cu}(\text{Ts3mepy})_2\text{phen}]$ $[\text{Cu}(\text{Ms3mepy})_2\text{bipy}]$ $[\text{Cu}(\text{Ms3mepy})_2\text{phen}]$	$[\text{Cu}(\text{Ts6mepy})_2\text{bipy}]$ $[\text{Cu}(\text{Ts6mepy})_2\text{phen}]$ $[\text{Cu}(\text{Ms6mepy})_2\text{bipy}]$ $[\text{Cu}(\text{Ms6mepy})_2\text{phen}]$
		

Table 7. Some short contacts between rings [$\text{\AA}$] (stacking) for the pentacoordinate compounds $[\text{CuL}_2\text{L}']$, $\text{L}' = \text{bipy}$ or phen

[Cu(Ts3mepy) ₂ phen]		[Cu(Ms3mepy) ₂ phen]		[Cu(Ms3mepy) ₂ bipy]	
N(31)–C(28)	3.607(6)	N(31)–C(212)	3.585(6)	N(31)–C(37)	3.680(4)
C(29)–C(31)	3.652(7)	N(32)–C(27)	3.680(5)	N(32)–C(212)	3.446(4)
C(33)–C(210)	3.599(8)	C(2)–C(311)	3.651(4)	N(32)–C(27)	3.752(3)
C(34)–C(211)	3.477(8)	C(2)–C(312)	3.663(4)	C(210)–C(37)	3.386(4)
C(37)–C(212)	3.705(8)	C(28)–C(311)	3.679(6)	C(210)–C(38)	3.697(5)
C(34)–C(210)	3.508(8)	C(29)–C(37)	3.683(6)	C(211)–C(39)	3.681(5)
C(211)–C(312)	3.599(7)	C(210)–C(34)	3.729(7)	C(212)–C(310)	3.680(4)
C(212)–C(312)	3.600(7)	C(211)–C(312)	3.611(6)		
C(212)–C(311)	3.471(7)	C(212)–C(31)	3.968(7)		
C(35)–C(211)	3.555(8)				

between 12 and 28% ($\tau = 0.12-0.28$, see Table 6).^[20] The oxygen atom occupies the apical position of the pyramid and the four nitrogen atoms of the three ligands form the basal plane. The copper atoms lies 0.203(2), 0.122(2), 0.114(1), and 0.069(2) $\text{\AA}$ out of this basal plane, respectively.

The Cu–N bond lengths are as expected for such complexes and do not warrant further comment. However, the Cu–O bonds [2.209(6) to 2.291(2) $\text{\AA}$], although slightly longer than in $[\text{Cu}(\text{Ts3mepy})_2\text{H}_2\text{O}]$, are shorter than the

Cu–O(apical) distances normally found in copper(II) square-pyramid complexes.^[18,23] This distance is remarkable since the sulfonamide groups are not good O-donors.

Complexes $[\text{Cu}(\text{Ts3mepy})_2\text{bipy}]$ and $[\text{Cu}(\text{Ts3mepy})_2\text{phen}]$ crystallize in the same space group, but their molecular arrangements are different due to a twist around the S(2)–N(22) bond (Figure 4 and Figure 5). Thus, in $[\text{Cu}(\text{Ts3mepy})_2\text{phen}]$, the planes of the 1,10-phenanthroline and the benzene ring of the monoanionic monodentate sulfonamide ligand are almost parallel, with a dihedral angle of

5.3(2)° and distances between rings of 3.471(7) Å. This disposition produces an intramolecular π,π -stacking interaction that stabilises the structure.^[24] This interaction does not seem to be present at an intermolecular level. Some short distances between rings are indicated in Table 7.

Conversely, complexes [Cu(Ms3mepy)₂bipy] and [Cu(Ms3mepy)₂phen] crystallize in the same space group, $P2_1/c$, and a intramolecular π,π -stacking interaction is found in both cases; the dihedral angles between rings are 3.2(1) and 1.41(8)°, respectively. However, the complexes are not identical, showing differences related to the spatial position of the mesitylene group, which is directed towards the π,π -stacking axis, or is twisted outward (Figure 8). Other parameters are also indicated in Table 7.

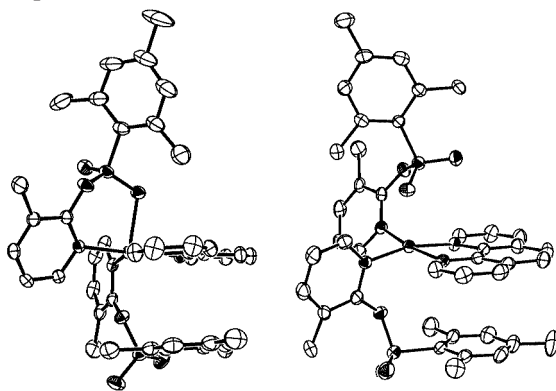


Figure 8. Spatial differences between [Cu(Ms3mepy)₂bipy] (left) and [Cu(Ms3mepy)₂phen] (right)

Structure of [Cu(Ms6mepy)₂phen]

This compound crystallizes in the triclinic $P\bar{1}$ space group with two chemically equivalent molecules in the asymmetric unit. Only one of the molecules is represented in Figure 9 (together with the atomic numbering pattern). Selected bond lengths and angles are given in Table 8.

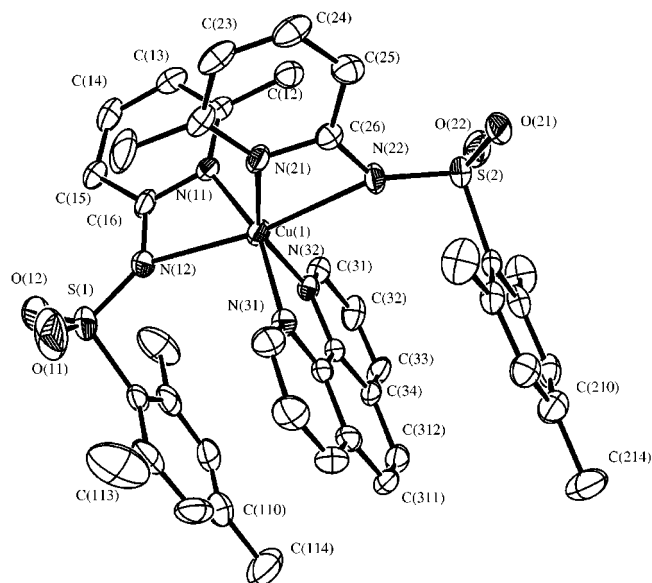


Figure 9. Molecular structure of [Cu(Ms6mepy)₂phen]

Table 8. Selected bond lengths [Å] and angles [°] for [Cu(Ms6mepy)₂phen]

Cu(1)–N(11)	1.985(6)	Cu(1)–N(31)	2.015(6)
Cu(1)–N(21)	2.023(6)	Cu(1)–N(32)	2.035(6)
Cu(1)–N(12)	2.357(6)	Cu(1)–N(22)	2.506(5)
Cu(2)–N(41)	1.983(6)	Cu(2)–N(51)	2.000(6)
Cu(2)–N(62)	2.001(6)	Cu(2)–N(61)	2.016(5)
Cu(2)–N(42)	2.413(6)	Cu(2)–N(52)	2.503(6)
N(11)–Cu(1)–N(31)	160.4(2)	N(11)–Cu(1)–N(21)	94.3(2)
N(31)–Cu(1)–N(21)	97.3(2)	N(11)–Cu(1)–N(32)	96.1(2)
N(31)–Cu(1)–N(32)	80.9(3)	N(21)–Cu(1)–N(32)	152.0(2)
N(11)–Cu(1)–N(12)	61.5(2)	N(31)–Cu(1)–N(12)	99.3(2)
N(21)–Cu(1)–N(12)	112.4(2)	N(32)–Cu(1)–N(12)	95.5(2)
N(11)–Cu(1)–N(22)	113.6(2)	N(31)–Cu(1)–N(22)	86.0(2)
N(21)–Cu(1)–N(22)	58.1(2)	N(32)–Cu(1)–N(22)	93.9(2)
N(12)–Cu(1)–N(22)	169.8(2)		
N(41)–Cu(2)–N(51)	93.1(2)	N(41)–Cu(2)–N(62)	158.9(3)
N(51)–Cu(2)–N(62)	97.6(2)	N(41)–Cu(2)–N(61)	95.6(2)
N(51)–Cu(2)–N(61)	156.5(3)	N(62)–Cu(2)–N(61)	81.7(2)
N(41)–Cu(2)–N(42)	60.0(2)	N(51)–Cu(2)–N(42)	115.1(3)
N(62)–Cu(2)–N(42)	99.0(2)	N(61)–Cu(2)–N(42)	88.1(2)
N(41)–Cu(2)–N(52)	115.4(2)	N(51)–Cu(2)–N(52)	58.3(3)
N(62)–Cu(2)–N(52)	85.6(2)	N(61)–Cu(2)–N(52)	98.3(2)
N(42)–Cu(2)–N(52)	172.7(2)		

The coordination behaviour of the anionic ligands in this complex is quite different from the other systems described here as the sulfonamide anionic ligands behave as (*N,N*)-bidentate ligands. A neutral 1,10-phenanthroline molecule acting as an (*N,N*)-donor completes the coordination sphere of the metal. Consequently, the coordination polyhedron around the copper(II) is best described as a highly distorted octahedron, CuN₆. There are several sources of distortion: Two Cu–N bond lengths are longer than the others, with a maximum of 2.506(5) Å. In addition, the anionic ligands form a four-membered chelate ring with angles of only 58.1(2) to 61.5(2)°. The theoretical equatorial plane is also highly distorted in that the dihedral angle between the planes formed by the central atom and the donors N_{phen}–Cu–N_{phen} and N_{py}–Cu–N_{py} is 32.66° [average values for the two molecules: 33.85(26) and 31.48(38)°].

Once again, significant intramolecular π,π stacking stabilisation is produced between the 1,10-phenanthroline unit and the benzene rings of the two sulfonamide ligands. This interaction does not seem to continue on an intermolecular level. The dihedral angles between the rings involved in this interaction are $\angle 6.2(4)^\circ$ (average 3.6°). The centres of the three rings are ca. 3.704 and 3.651 Å apart. Some short distances between rings are indicated in Table 9.

Spectroscopic and Magnetic Studies

The IR spectra of the complexes do not show the band attributable to $\nu(\text{N–H})$, which in the free ligand appears at 3248–3222 cm^{−1}. This change confirms that the hydrogen atom of the amide group is lost during electrolysis. The bands in the spectra of the ligands in the range 1594–1612 cm^{−1}, due to the $\nu(\text{C=N})$ absorption, appear in similar po-

Table 9. Selected short contacts between rings [Å] (stacking) for [Cu(Ms6mepy)₂phen]

N(31)–C(18)	3.775(10)	N(31)–C(17)	3.798(10)
N(31)–C(212)	3.895(9)	N(31)–C(27)	3.916(8)
N(32)–C(112)	3.623(9)	N(32)–C(17)	3.888(9)
C(18)–C(36)	3.655(10)	C(19)–C(37)	3.530(14)
C(111)–C(34)	3.521(11)	C(110)–C(312)	3.597(13)
C(112)–C(35)	3.634(10)	C(111)–C(35)	3.656(11)
C(28)–C(35)	3.667(10)	C(29)–C(312)	3.613(11)
C(211)–C(37)	3.692(11)	C(29)–C(311)	3.664(11)
N(62)–C(47)	3.706(9)	C(210)–C(311)	3.624(12)
C(48)–C(610)	3.625(10)	N(61)–C(512)	3.726(10)
C(49)–C(68)	3.559(13)	N(62)–C(48)	3.647(9)
C(410)–C(612)	3.688(14)	C(410)–C(67)	3.537(12)
C(412)–C(65)	3.630(10)	C(59)–C(612)	3.616(13)
C(511)–C(63)	3.616(13)	C(511)–C(64)	3.546(12)
C(510)–C(64)	3.548(11)	C(510)–C(611)	3.523(12)

sitions in the complexes except when the ligands Ts6mepy[−] and Ms6mepy[−] are present, in which case the bands are shifted to lower frequencies due to coordination through the sulfonamide nitrogen atom. The bands of the ligands at 1338–1369 cm^{−1}, attributable to $\nu_{\text{as}}(\text{S}=\text{O})$, are also seen for the complexes with Ts3mepy[−] and Ms3mepy[−] but in these cases they are shifted to slightly lower frequencies due to the coordination.

In addition, the IR spectra of the mixed complexes show absorptions that are typical of coordinated 2,2'-bipyridine (764 and 736 cm^{−1}) and 1,10-phenanthroline (1520, 850, and 720 cm^{−1}).

The electronic reflectance spectrum of the pentacoordinate complex [Cu(Ts3mepy)₂H₂O] shows a very broad band, probably a multicomponent band, at 15800 with a shoulder at ca. 11800 cm^{−1}, a situation in accord with a pseudo-square planar pyramidal environment forming a [CuN₂O₃] chromophore.^[25]

The electronic reflectance spectra of [Cu(Ts3mepy)₂phen], [Cu(Ts3mepy)₂bipy], [Cu(Ms3mepy)₂phen], and [Cu(Ms3mepy)₂bipy] show two broad bands in the range 16300–15900 cm^{−1} and 12300–10600 cm^{−1}. This is similar to the spectra of copper(II) complexes involving a [CuN₄O] chromophore.^[26]

The electronic reflectance spectrum of [Cu(Ms6mepy)₂phen] shows two bands at 14430 and 10955 cm^{−1}, which are similar to those found for [Cu(Ms6mepy)₂bipy], [Cu(Ts6mepy)₂bipy], and [Cu(Ts6mepy)₂phen], suggesting an octahedral [CuN₆] chromophore for all these compounds.^[27]

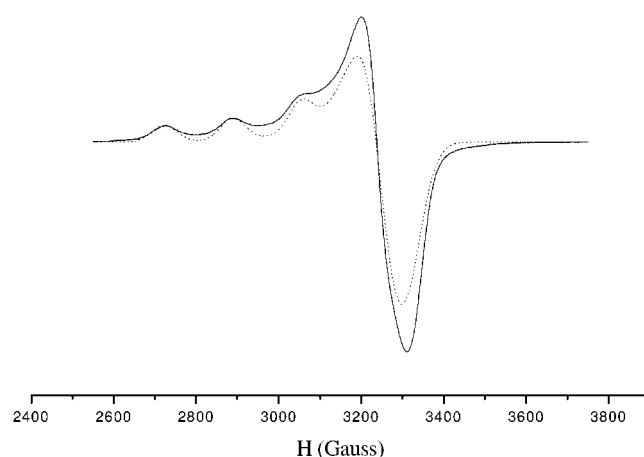
The magnetic moments at room temperature are close to 1.8 B.M. in all cases, as expected for d⁹ systems.

The X-band spectra of polycrystalline samples of the complexes were recorded at room temperature. Table 10 shows the EPR parameters of the ternary complexes obtained by simulation.^[28] As an example, Figure 10 shows both the obtained and simulated EPR spectrum of [Cu(Ms6mepy)₂phen].

All the spectra are axial with similar EPR parameters so that it can be predicted due to the similarity of the sulfona-

Table 10. EPR and RD parameters for the complexes (sh: shoulder)

Compound	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$\tilde{\nu}$ [cm ^{−1}]	
[Cu(Ts3mepy) ₂ (H ₂ O)]	2.25	2.11	140	15800	11820(sh)
[Cu(Ts3mepy) ₂ bipy]	2.26	2.06	150	15975	10640
[Cu(Ts3mepy) ₂ phen]	2.21	2.07	156	16315	12195
[Cu(Ms3mepy) ₂ bipy]	2.23	2.07	150	16130	11765
[Cu(Ms3mepy) ₂ phen]	2.26	2.07	155	16315	12300
[Cu(Ts6mepy) ₂ bipy]	2.26	2.08	—	13515	9320
[Cu(Ts6mepy) ₂ phen]	2.26	2.08	—	13280	10640
[Cu(Ms6mepy) ₂ bipy]	2.26	2.06	163	14165	11200
[Cu(Ms6mepy) ₂ phen]	2.26	2.08	166	14430	10955

Figure 10. EPR Spectra in X-band of the complex [Cu(Ms6mepy)₂phen] (solid line) and its simulation (dotted line) as a powder at room temperature

midate ligands and the bipy and phen. Bertini^[29] has suggested that $A_{\parallel}$ may be a measure of the coordination polyhedron around copper(II). Accordingly $A_{\parallel}$ from 120 to 150 G indicates a square-pyramidal geometry while values of 160–200 G correspond to a square planar or six-coordinate stereochemistry. The $A_{\parallel}$ s of [Cu(Ts3mepy)₂(H₂O)], [Cu(Ts3mepy)₂bipy] and [Cu(Ms3mepy)₂bipy] suggest a square-pyramidal arrangement, in agreement with their crystal structures. The $A_{\parallel}$ s of [Cu(Ms6mepy)₂phen] indicate a six-coordinate geometry, which agrees with the crystal structure. The complexes [Cu(Ts3mepy)₂phen] and [Cu(Ms3mepy)₂phen] are in the limit between the pentacoordinate and the six-coordinate environment; their crystal structures both show a distorted square-pyramidal geometry. From the $A_{\parallel}$ s of [Cu(Ms6mepy)₂bipy] we propose a six-coordinate around copper(II). Similar conclusions were obtained from the spectroscopic data.

Conclusion

The most important feature of these complexes is the coordinative behaviour of the anionic ligand and the presence or absence of π,π -stacking (Table 11).

The ligands behave in a (N,O) bidentate way with a substituent at position 3. However, for a substituent in position

Table 11. Conclusions

Complex	Behaviour of the ligands		Coligand	Environment around Cu atom	Geometry	π - π stacking
	L ¹	L ²				
[Cu(Ts3mepy) ₂ (H ₂ O)]	bidentate-(N,O)	bidentate-(N,O)	monodentate-O	[CuN ₂ O ₃]	Square pyramid (τ = 0.07)	no
[Cu(Ts3mepy) ₂ bipy]	monodentate-N	bidentate-(N,O)	bidentate-(N,N)	[CuN ₄ O]	Square pyramid (τ = 0.28)	no
[Cu(Ts3mepy) ₂ phen]	monodentate-N	bidentate-(N,O)	bidentate-(N,N)	[CuN ₄ O]	Square pyramid (τ = 0.18)	yes
[Cu(Ms3mepy) ₂ phen]	monodentate-N	bidentate-(N,O)	bidentate-(N,N)	[CuN ₄ O]	Square pyramid (τ = 0.12)	yes
[Cu(Ms3mepy) ₂ bipy]	monodentate-N	bidentate-(N,O)	bidentate-(N,N)	[CuN ₄ O]	Square pyramid (τ = 0.18)	yes
[Cu(Ts6mepy) ₂ bipy]	bidentate-(N,N)	bidentate-(N,N)	bidentate-(N,N)	[CuN ₆]	Octahedral	
[Cu(Ts6mepy) ₂ phen]	bidentate-(N,N)	bidentate-(N,N)	bidentate-(N,N)	[CuN ₆]	Octahedral	
[Cu(Ms6mepy) ₂ phen]	bidentate-(N,N)	bidentate-(N,N)	bidentate-(N,N)	[CuN ₆]	Octahedral	yes
[Cu(Ms6mepy) ₂ bipy]	bidentate-(N,N)	bidentate-(N,N)	bidentate-(N,N)	[CuN ₆]	Octahedral	

6, they behave in a (*N,N*) bidentate way. Probably, the difference can be traced to a steric effect. A substituent in position 3 pushes the sulfonyl group towards the metal, and induces (*N,O*) bidentate behaviour.

In addition, when the coligand is 1,10-phenanthroline the third ring allows a π , π -stacking, either with the toluene ring or the mesitylene ring. When the coligand is 2,2'-bipyridine, π , π -stacking is only produced when the benzene ring is substituted by three methyl groups. This could be due to the electron-releasing effect of the three methyl groups in the ring, together with the increasing size of the group.

Experimental Section

Acetonitrile, dichloromethane, 2-amino-3-picoline, 2-amino-6-picoline, *p*-toluenesulfonyl chloride, 2-mesitylenesulfonyl chloride, 2,2'-bipyridine, 1,10-phenanthroline monohydrate, sodium carbonate, magnesium sulfate, and all other reagents were commercial products and were used as supplied. Copper (Aldrich) was used as 2 × 2 cm plates.

Preparation of the Ligands

Ligands were prepared by reaction of the corresponding amine and the sulfonyl chloride in a 1:1 ratio. Details are given for a representative example.

HMs3mepy: An aqueous solution of sodium carbonate (1.95 g, 18.4 mmol in 20 mL) was added dropwise to a solution of 2-amino-3-picoline (2.0 g, 18.4 mmol) and 2-mesitylenesulfonyl chloride (4.05 g, 18.4 mmol) dissolved in dichloromethane. The reaction mixture was then stirred overnight and water (100 mL) was added. The organic layer was then separated and dried over anhydrous magnesium sulfate. The solvent was evaporated and the crude product, an oil, was treated with ethanol. The resulting white solid was isolated by filtration and identified as HMs3mepy; yield 16.7%. C₁₅H₁₈N₂O₂S (%): calcd. C 62.1, H 6.2, N 9.6, S 11.0; found C 61.3, H 6.0, N 9.3, S 11.2. ¹H NMR (CDCl₃, ppm): δ = 2.15 [s, 3 H, CH₃(py)]; 2.25 [s, 3 H, CH₃(*p*-mesityl)]; 2.71 [s, 6 H, CH₃(*o*-mesityl)]; 6.47 (t, 1 H, py); 6.89 (s, 2 H, tolyl); 7.36 (d, 1 H, py); 7.42 (d, 1 H, py); 12.33 (b, 1 H, NH). IR (KBr, cm⁻¹): 3222 (m), 2940 (w), 1633 (w), 1595 (s), 1544 (s), 1375 (w), 1338 (s), 1259 (m), 1098 (s), 1047 (m), 780 (m), 676 (m). EI MS: *m/z* (%): 291 (100) [M⁺]; 108 (10) [M⁺ - {O₂S-mesityl}].

HMs6mepy: Yield 42.1%. C₁₅H₁₈N₂O₂S (%): calcd. C 62.1, H 6.2, N 9.6, S 11.0; found C 61.3, H 6.4, N 9.5, S 10.9. ¹H NMR (CDCl₃,

ppm): δ = 2.24 [s, 3 H, CH₃(*p*-mesityl)]; 2.37 [s, 3 H, CH₃(py)]; 2.69 [s, 6 H, CH₃(*o*-mesityl)]; 6.55 (d, 1 H, py); 6.74 (d, 1 H, py); 6.88 (s, 2 H, tolyl); 7.37 (t, 1 H, py); 9.40 (b, 1 H, NH). IR (KBr, cm⁻¹): 3236 (w), 2931 (w), 1617 (s), 1533 (m), 1457 (m), 1363 (vs), 1290 (m), 1136 (s), 1063 (w), 834 (m), 656 (m). EI MS: *m/z* (%): 291(4) [M⁺]; 108 (13) [M⁺ - {O₂S-mesityl}].

HTs3mepy: Yield 26.7%. C₁₃H₁₄N₂O₂S (%): calcd. C 59.5, H 5.4, N 10.7, S 12.2; found C 58.7, H 5.7, N 10.2, S 11.8. ¹H NMR (CDCl₃, ppm): δ = 2.15 [s, 3 H, CH₃(py)]; 2.35 [s, 3 H, CH₃(tolyl)]; 6.50 (t, 2 H, tolyl); 7.21 (d, 1 H, py); 7.40 (d, 1 H, py); 7.49 (d, 1 H, py); 7.85 (d, 2 H, tolyl); 12.14 (b, 1 H, NH). IR (KBr, cm⁻¹): 3248 (m), 2920 (w), 1593 (s), 1543 (s), 1399 (m), 1371 (m), 1342 (s), 1255 (m), 1126 (s), 1080 (m), 963 (m), 767 (w), 683 (m), 570 (w). EI MS: *m/z* (%): 262 (8) [M⁺]; 108 (20) [M⁺ - {O₂S-tolyl}].

HTs6mepy: Yield 37.5%. C₁₃H₁₄N₂O₂S (%): calcd. C 59.5, H 5.4, N 10.7, S 12.2; found C 58.8, H 5.6, N 10.6, S 12.3. ¹H NMR (CDCl₃, ppm): δ = 2.36 [s, 3 H, CH₃(tolyl)]; 2.41 [s, 3 H, CH₃(py)]; 6.60 (d, 1 H, py); 7.06 (d, 1 H, py); 7.22 (d, 2 H, tolyl); 7.46 (t, 1 H, py); 7.79 (d, 2 H, tolyl); 9.95 (b, 1 H, NH). IR (KBr, cm⁻¹): 3231 (w), 3052 (w), 2958 (w), 1613 (vs), 1534 (m), 1369 (s), 1252 (m), 1135 (s), 1089 (m), 855 (m), 787 (m), 661 (m), 572 (m). EI MS: *m/z* (%): 262 (6) [M⁺]; 108 (3) [M⁺ - {O₂S-tolyl}].

Preparation of Complexes. General Procedure: The complexes were obtained by an electrochemical procedure.^[30] The cell consisted of a tall-form beaker (100 mL) fitted with a rubber bung through which the electrochemical leads entered. An acetonitrile solution of either the ligand or the ligand/coligand (1,10-phenanthroline-monohydrate or 2,2'-bipyridine) mixture containing tetraethylammonium perchlorate (ca. 20 mg) as electrolyte was electrolysed using a platinum wire as the cathode and a copper plate as the sacrificial anode. Direct current was supplied by a purpose-built d.c. power supply. The applied voltages (5–15 V) allowed sufficient current flow for smooth dissolution of the copper metal. The current was maintained at 10 mA for one hour. In all cases, hydrogen was evolved at the cathode. These cells can be summarised as Cu₍₊₎/CH₃CN + HL + L'/Pt₍₋₎, where L' is 2,2'-bipyridine or 1,10-phenanthroline.

After one hour of electrolysis, the resultant clear green solutions were filtered to remove any particles of metal and then left to concentrate. This procedure afforded crystalline products in good yield. The solids were then washed with acetonitrile and diethyl ether and dried at room temperature.

[Cu(Ts3mepy)₂H₂O]: Electrochemical oxidation of a copper anode in a solution of the ligand *N*-(3-methyl-2-pyridyl)-*p*-toluenesulfonamide, (0.19 g, 0.75 mmol) in acetonitrile (50 cm³), at 12 V and

10 mA for 1 h, dissolved copper (25 mg), $E_f = 1.05 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{26}\text{H}_{28}\text{CuN}_4\text{O}_5\text{S}_2$ (%): calcd. C 51.7, N 9.3, H 4.7, S 10.6; found C 51.2, N 9.4, H 4.5, S 10.3. IR (KBr, cm^{-1}): 3444 (m), 2922 (w), 1593 (s), 1419 (s), 1336 (w), 1265 (m), 1133 (s), 1090 (m), 853 (w), 814 (w), 665 (m), 587 (m), 546 (m).

[Cu(Ts3mepy)₂bipy]: Electrolysis of a solution of the ligand (0.19 g, 0.75 mmol) and 2,2'-bipyridine (0.58 g, 0.37 mmol) in acetonitrile, (50 cm^3) at 10 V and 10 mA for 1 h dissolved copper (26 mg) from the anode, $E_f = 1.10 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{36}\text{H}_{34}\text{CuN}_4\text{O}_4\text{S}_2$ (%): calcd. C 58.3, N 11.3, H 4.6, S 8.6; found C 57.8, N 11.3, H 4.8, S 8.4. IR (KBr, cm^{-1}): 3441 (m), 2922 (w), 1606 (m), 1445 (w), 1416 (s); 1327 (m), 1247 (m), 1128 (m), 1085 (m), 772 (m), 737 (w), 659 (m), 587 (m), 550 (m).

[Cu(Ts3mepy)₂phen]: A solution of the ligand (0.19 g, 0.75 mmol) and 1,10-phenanthroline (0.07 g, 0.37 mmol) in acetonitrile (50 cm^3) was electrolyzed at 8 V and 10 mA for 1 hour; copper metal (22 mg) was dissolved from the anode, $E_f = 0.93 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{38}\text{H}_{34}\text{CuN}_4\text{O}_4\text{S}_2$ (%): calcd. C 59.4, N 10.9, H 4.7, S 8.3; found C 59.5, N 11.1, H 4.7, S 8.3. IR (KBr, cm^{-1}): 3445 (m), 2922 (w), 1596 (m), 1457 (s), 1339 (s), 1135 (s), 1097 (m), 855 (m), 769 (w), 731 (w), 660 (w), 577 (w), 550 (w).

[Cu(Ms3mepy)₂bipy]: A solution of the ligand *N*-(3-methyl-2-pyridyl)mesitylenesulfonamide (0.22 g, 0.75 mmol) and 2,2'-bipyridine (0.58 g, 0.37 mmol) in acetonitrile (50 cm^3) was electrolyzed at 14 V and 10 mA for 1 hour; copper (27 mg) was dissolved from the anode, $E_f = 1.13 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{40}\text{H}_{42}\text{CuN}_4\text{O}_4\text{S}_2$ (%): calcd. C 60.1, N 10.5, H 5.3, S 8.0; found C, 59.5, N 10.2, H 5.3, S 8.1. IR (KBr, cm^{-1}): 3443 (m), 2931 (w), 1605 (m), 1416 (s), 1327 (m), 1228 (m), 1117 (s), 1057 (w), 770 (m), 728 (w), 687 (m), 593 (w), 521 (w).

[Cu(Ms3mepy)₂phen]: Electrochemical oxidation of a copper anode in a solution of the ligand (0.22 g, 0.75 mmol) and 1,10-phenanthroline (0.07 g, 0.37 mmol) in acetonitrile (50 cm^3), at 14 V and 10 mA for 1 h dissolved copper (22 mg), $E_f = 0.93 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{42}\text{H}_{42}\text{CuN}_4\text{O}_4\text{S}_2$ (%): calcd. C 61.1, N 10.2, H 5.1, S 7.8; found C 61.1, N 10.4, H 5.2, S 7.6. IR (KBr, cm^{-1}): 3425 (m), 2930 (w), 1594 (m), 1512 (m), 1416 (s), 1319 (m), 1121 (s), 845 (m), 724 (m), 683 (w), 593 (w), 532 (w).

[Cu(Ts6mepy)₂bipy]: A similar experiment to those described above (10 V, 10 mA, 1 h) with *N*-(6-methyl-2-pyridyl)-*p*-toluenesulfonamide (0.19 g, 0.75 mmol) and 2,2'-bipyridine (0.58 g, 0.37 mmol) in acetonitrile (50 cm^3) led to the dissolution of 25 mg of metal, $E_f = 1.05 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{36}\text{H}_{34}\text{CuN}_4\text{O}_4\text{S}_2$ (%): calcd. C 58.3, N 11.3, H 4.6, S 8.6; found C 57.9, N 11.6, H 4.4, S 8.5. IR (KBr, cm^{-1}): 3445 (m), 2922 (w), 1596 (m), 1457 (s), 1339 (s), 1135 (s), 1097 (m), 855 (m), 769 (w), 731 (w), 660 (w), 577 (w), 550 (w).

[Cu(Ts6mepy)₂phen]: A similar experiment to those described above (12 V, 10 mA, 1 h) with HTs6mepy (0.19 g, 0.75 mmol) and 1,10-phenanthroline (0.07 g, 0.37 mmol) in acetonitrile (50 cm^3) led to the dissolution of metal (22 mg), $E_f = 0.93 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{38}\text{H}_{34}\text{CuN}_4\text{O}_4\text{S}_2$ (%): calcd. C 59.4, N 10.9, H 4.7, S 8.3; found C 58.8, N 11.4, H 4.5, S 7.9. IR (KBr, cm^{-1}): 3441 (m), 2924 (w), 1596 (m), 1518 (w), 1457 (m), 1339 (m), 1266 (m), 1134 (m), 1096 (m), 852 (w), 723 (w), 665 (m), 578 (m), 551 (w).

[Cu(Ms6mepy)₂bipy]: In similar fashion to above (12 V, 10 mA, 1 h), *N*-(6-methyl-2-pyridyl)-2-mesitylenesulfonamide (0.22 g, 0.75 mmol) and 2,2'-bipyridine (0.58 g, 0.37 mmol) in acetonitrile (50 cm^3) led to the dissolution of 28 mg of metal, $E_f = 1.18 \text{ mol}\cdot\text{F}^{-1}$. $\text{C}_{40}\text{H}_{42}\text{CuN}_4\text{O}_4\text{S}_2$ (%): calcd. C 60.1, N 10.5, H 5.3, S

Table 12. Summary of crystal data and structure refinement

Identification code:	HMs3mepy	[Cu(Ts3mepy) ₂ H ₂ O]	[Cu(Ts3mepy) ₂ bipy].	[Cu(Ts3mepy) ₂ phen]
Empirical formula	$\text{C}_{30}\text{H}_{36}\text{N}_4\text{O}_4\text{S}_2$	$\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_5\text{S}_2\text{Cu}$	$\text{C}_{36}\text{H}_{34}\text{N}_6\text{O}_4\text{S}_2\text{Cu}$	$\text{C}_{38}\text{H}_{34}\text{N}_6\text{O}_4\text{S}_2\text{Cu}$
Molecular mass	580.75	604.18	742.35	766.37
Temperature	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $C2/c$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
Unit cell dimensions	$a = 15.069(2) \text{ Å}$ $b = 8.0862(11) \text{ Å}$ $c = 24.651(3) \text{ Å}$ $\alpha = 90^\circ$ $\beta = 102.765(3)^\circ$ $\gamma = 90^\circ$	$a = 16.6262(15) \text{ Å}$ $b = 6.0343(5) \text{ Å}$ $c = 27.530(3) \text{ Å}$ $\alpha = 90^\circ$ $\beta = 103.112(2)^\circ$ $\gamma = 90^\circ$	$a = 17.346(3) \text{ Å}$ $b = 9.2519(14) \text{ Å}$ $c = 24.083(3) \text{ Å}$ $\alpha = 90^\circ$ $\beta = 114.640(8)^\circ$ $\gamma = 90^\circ$	$a = 10.7185(12) \text{ Å}$ $b = 10.9915(13) \text{ Å}$ $c = 17.6002(19) \text{ Å}$ $\alpha = 106.300(2)^\circ$ $\beta = 102.900(3)^\circ$ $\gamma = 97.734(2)^\circ$
Volume	2929.5(7) Å ³	2690.0(4) Å ³	3513.0(9) Å ³	1896.3(4) Å ³
Z, calculated density	4, 1.317 Mg/m ³	4, 1.492 Mg/m ³	2, 1.404 Mg/m ³	2, 1.342 Mg/m ³
Absorption coefficient	0.224 mm ⁻¹	1.011 mm ⁻¹	0.789 mm ⁻¹	0.733 mm ⁻¹
$F(000)$	1232	1252	1540	794
Crystal size	0.41 × 0.47 × 0.50 mm	0.8 × 0.46 × 0.62 mm	0.03 × 0.10 × 0.14 mm	0.9 × 0.1 × 0.16 mm
Theta range for data collection	2.77 to 28.05°	1.52 to 28.01°	1.29 to 28.09°	1.97 to 28.05°
Index ranges	$-19 \leq h \leq 18$, $-9 \leq k \leq 10$, $-32 \leq l \leq 28$	$-21 \leq h \leq 21$, $-7 \leq k \leq 6$, $-29 \leq l \leq 36$	$-22 \leq h \leq 22$, $-12 \leq k \leq 12$, $-31 \leq l \leq 18$	$-13 \leq h \leq 14$, $-13 \leq k \leq 14$, $-23 \leq l \leq 17$
Reflections collected/unique	8866/ 3441 [$R(\text{int}) = 0.0279$]	14844/6056 [$R(\text{int}) = 0.0364$]	17080/7613 [$R(\text{int}) = 0.1615$]	11011/7676 [$R(\text{int}) = 0.0600$]
Completeness to 2 θ	96.5%	93.3%	83.9%	83.4%
Data/restraints/parameters	3441/0/209	6056/0/355	7613/0/426	7676/0/464
Goodness-of-fit on F^2	1.043	0.923	0.697	0.740
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0446$, $wR_2 = 0.1174$	$R_1 = 0.0404$, $wR_2 = 0.0911$	$R_1 = 0.0570$, $wR_2 = 0.1005$	$R_1 = 0.0572$, $wR_2 = 0.0900$
R indices (all data)	$R_1 = 0.0590$, $wR_2 = 0.1240$	$R_1 = 0.0797$, $wR_2 = 0.1017$	$R_1 = 0.3440$, $wR_2 = 0.1974$	$R_1 = 0.1689$, $wR_2 = 0.1089$
Largest diff. peak and hole	0.256 and $-0.422 \text{ e} \cdot \text{Å}^{-3}$	0.397 and $-0.312 \text{ e} \cdot \text{Å}^{-3}$	0.426 and $-0.343 \text{ e} \cdot \text{Å}^{-3}$	0.266 and $-0.269 \text{ e} \cdot \text{Å}^{-3}$

Table 13. Summary of crystal data and structure refinement

Identification code:	[Cu(Ms3mepy) ₂ bipy]	[Cu(Ms3mepy) ₂ phen]	[Cu(Ms6mepy)phen] ₂
Empirical formula	C ₄₀ H ₄₂ N ₆ O ₄ S ₂ Cu	C ₄₂ H ₄₂ N ₆ O ₄ S ₂ Cu	C ₄₂ H ₄₂ N ₆ O ₄ S ₂ Cu
Molecular mass	798.46	822.48	822.48
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	triclinic, <i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 17.1798(11) Å <i>b</i> = 15.6081(10) Å <i>c</i> = 15.5389(9) Å α = 90° β = 105.6420(10)° γ = 90°	<i>a</i> = 16.2855(12) Å <i>b</i> = 15.8753(11) Å <i>c</i> = 15.0249(11) Å α = 90° β = 96.897(2) deg. γ = 90°	<i>a</i> = 15.370(5) Å <i>b</i> = 16.143(5) Å <i>c</i> = 17.532(5) Å α = 109.564(5)° β = 92.724(5)° γ = 98.831(5)°
Volume	4012.4(4) Å ³	3856.4(5) Å ³	4027(2) Å ³
Z, calculated density	4, 1.322 Mg/m ³	4, 1.417 Mg/m ³	2, 1.357 Mg/m ³
Absorption coefficient	0.696 mm ⁻¹	0.726 mm ⁻¹	0.695 mm ⁻¹
<i>F</i> (000)	1668	1716	1716
Crystal size	0.15 × 0.23 × 0.54 mm	0.44 × 0.12 × 0.12 mm	0.31 × 0.25 × 0.22 mm
Theta range for data collection	1.79 to 28.02°	1.80 to 28.02°	1.24 to 26.48°
Index ranges	−22 ≤ <i>h</i> ≤ 22, −20 ≤ <i>k</i> ≤ 20, −14 ≤ <i>l</i> ≤ 20	−20 ≤ <i>h</i> ≤ 21, −20 ≤ <i>k</i> ≤ 19, −19 ≤ <i>l</i> ≤ 15	−17 ≤ <i>h</i> ≤ 19, −20 ≤ <i>k</i> ≤ 17, −21 ≤ <i>l</i> ≤ 21
Reflections collected/unique	23177/9157 [R(int) = 0.0578]	22031/8786 [R(int) = 0.0599]	33835/16311 [R(int) = 0.0788]
Completeness to 2θ	94.3%	94.3%	97.9%
Data/restraints/parameters	9157/0/486	8786/0/496	16311/5/1007
Goodness-of-fit on <i>F</i> ²	0.862	0.871	0.934
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.0893	<i>R</i> ₁ = 0.0528, <i>wR</i> ₂ = 0.1023	<i>R</i> ₁ = 0.0703, <i>wR</i> ₂ = 0.1779
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0991, <i>wR</i> ₂ = 0.1009	<i>R</i> ₁ = 0.1505, <i>wR</i> ₂ = 0.1222	<i>R</i> ₁ = 0.2359, <i>wR</i> ₂ = 0.2432
Largest diff. peak and hole	0.392 and −0.264 e·Å ⁻³	0.448 and −0.291 e·Å ⁻³	0.891 and −0.628 e·Å ⁻³

8.0; found C 59.7, N 10.4, H 5.2, S 7.8. IR (KBr, cm⁻¹): 3443 (m), 2931 (w), 1598 (s), 1457 (s), 1343 (s), 1251 (m), 1125 (s), 1083 (m), 843 (m), 768 (w), 732 (w), 671 (w), 587 (w), 535 (w).

[Cu(Ms6mepy)₂phen]: By a similar procedure (15 V, 10 mA, 1 h), HMs6mepy, (0.22 g, 0.75 mmol) and 1,10-phenanthroline (0.07 g, 0.37 mmol) in acetonitrile (50 cm³) led to the dissolution of metal (25 mg), *E*_f = 1.05 mol·F⁻¹. C₄₂H₄₂CuN₆O₄S₂ (%): calcd. C 61.1, N 10.2, H 5.2, S 7.8; found C 60.8, N 10.1, H 5.2, S 7.6. IR (KBr, cm⁻¹): 3445 (m), 2931 (w), 1594 (m), 1519 (w), 1457 (m), 1344 (m), 1250 (w), 1124 (s), 1082 (m), 845 (m), 722 (w), 689 (w), 588 (w), 533 (w).

Physical Measurements: The C, N, H, and S contents of the compounds were determined on a Carlo–Erba EA 1108 microanalyser. IR spectra in the solid state were recorded as KBr mulls on a Bruker Vector-22 spectrophotometer. The ¹H NMR spectra of the ligands were recorded on a Bruker ARX-400 MHz spectrometer using CDCl₃ as solvent. Solid-state electronic spectra were recorded on a Shimadzu UV 3101 PC. Magnetic measurements were made using a DMS VSM 1160. EI (70 eV, 250 °C), and LSI mass spectra were recorded on a VG Autospec-M Micromass, using 2-nitrobenzyl alcohol (2-NBA) as matrix material. EPR measurements on solid samples were recorded on a Bruker EMX spectrometer, using frequencies between 9400 and 9800 MHz (X-band).

X-ray Crystallographic Study: Data collections were taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo-*K*_α radiation. Absorption corrections were carried out using SADABS.^[31]

All the structures were solved by direct methods and refined by full-matrix least-squares based on *F*².^[32] All non-hydrogen atoms were refined with anisotropic displacement parameters. For

HMs3mepy the hydrogen atoms (except those of the methyl groups) were located on a difference electron density map and refined with isotropic displacement parameters. For the complexes, hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters, except for those of the water molecule of [Cu(Ts3mepy)₂H₂O], which were located and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography.^[33] Details of crystal data and structural refinements are given in Tables 12 and 13.

CCDC 187516 and 209128–209133 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].

Acknowledgments

This work was supported by the FLUNTA DE ALICIA, under the grant PGIDT00PX120305PR, the Ministerio de Ciencia y Tecnología (Spain), under grant BQU2002–01819, and the Universidade de Vigo, under grant C221 122F 64102.

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Received June 4, 2003

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Published Online December 19, 2003