Different Coordinative (N, N) and (N, O) Bidentate Behaviour of N-2-Pyridyl-Sulfonamides. Electrochemical Synthesis and Characterization of Cadmium(II) Complexes

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 60th Birthday

Abstract. Electrochemical oxidation of cadmium in an acetonitrile solution of N-2-pyridyl-sulfonamides (HL) afforded cadmium coordination compounds of composition [CdL2]. Heteroleptic complexes of composition $[CdL_2L']$ (L' = 2,2'-bipyridine or 1,10-phenanthroline) were obtained when the coligand L' was added to the electrolytic phase. The crystal structures of several compounds have been determined by X-ray diffraction. In all cases the cadmium atom is hexacoordinated, but the coordinative behaviour of the N-2-pyridyl-sulfonamide ligand depends on the location of the substituents in the pyridyl ring. When the substituent is in position 3, the ligands act as N,O-donors. In all other cases, the ligands act as N,N'-bidentate systems.

Keywords: Cadmium; Amide ligands; Electrochemical synthesis; Crystal structure

Unterschiedliches, zweizähniges Koordinationsverhalten (N,N) und (N,O) von N-2-pyridyl-Sulfonamiden. Elektrochemische Synthesen und Charakterisierung von Cadmium(II)-Komplexen

Inhaltsübersicht. Die elektrochemische Oxidation von Cadmium in Acetonitrillösungen von N-pyridyl-Sulfonamiden (HL) führt zur Bildung von Koordinationsverbindungen des Cadmiums der Zusammensetzung [CdL₂]. Heteroleptische Komplexe [CdL₂L'] (L' = 2,2'-Dipyridin oder 1,10-Phenanthrolin) werden in Gegenwart des Koliganden L' im Elektrolyten erhalten. Die Kristallstrukturen

1 Introduction

Recently, the chemistry of metal complexes containing amide ligands has been a subject of great interest. The reason for it stems from the fact that they are easily made, and variations of the substituents are facile, providing the possibility of changing almost at will their bite angle and

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mehrerer Verbindungen wurden röntgenographisch ermittelt. In allen Fällen ist das Cadmiumatom sechsfach koordiniert, jedoch hängt das koordinative Verhalten von der Stellung der Substituenten am Pyridylring ab. Substitution in 3-Stellung führt zur N,O-Koordination, in allen anderen Fällen zu N,N'-Chelatbildung.

their steric hindrance. The chemistry of metal complexes containing pyridine-functionalized amido ligands of the type showed below, Scheme 1, has received a lot of attention [1-5].

Scheme 1

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It is believed that the presence of bulky substituents on these ligands stabilizes the metal complexes.

Consequently, it was decided to study the chemistry of the metal complexes of sulfonyl-2-pyridine-amines. These ligands, 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 the process of ligand deprotonation easier.



Scheme 2

It has been found that these ligands can coordinate to the metal atom in several different ways, Scheme 3.





Coordination modes I and II have been found in zinc compounds. However, it is worth noting that in the case of the complex showing coordination mode I, a weak interaction between the metal and the exocyclic nitrogen atom is present [6]. In the case of the compound showing coordination mode II, a weak interaction between the zinc and the pyridine nitrogen atom is found [7]. Coordination mode III is the most common, and it has been found in cobalt(II) [8], nickel(II) [9] and cadmium (II) [10] complexes. To this moment, coordination mode IV was only found in copper(II) [7, 11] and silver(I) [7, 12] complexes. Coordination modes V and VI were found in a polymer compound of cadmium(II) [10] and the coordination mode VII was only found, at the moment, in silver(I) complexes [7].

The work described in this paper deals with the electrochemical synthesis and characterization of cadmium(II) complexes [CdL₂]. HL stands for phenylsulfonyl-2-pyridyl amine derivatives containing methyl substituent groups in both phenyl and pyridine rings, Scheme 4. In addition, ternary 2,2'-bipyridine and 1,10-phenanthroline adducts [CdL₂bipy] or [CdL₂phen] are also described.

| R ¹ | Code | \mathbb{R}^1 | R ² |
|------------------|----------|-----------------------|----------------|
| o=s=o | HTs3mepy | 4-Me | 3Me |
| 'n ∐ | HTs6mepy | 4–Me | 6-Me |
| R ² - | HMs3mepy | 2,4,6–Me ₃ | 3-Me |
| ~ | HMs6mepy | 2,4,6-Me ₃ | 6–Me |
| HL | | | |

2 Results and Discussion

Cadmium complexes with N-2-pyridyl-sulfonamides, as well as their adducts with 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen), were easily prepared in good yields by the simple one-step electrochemical method. In all cases, the product formed was easily isolated as a crystalline species from the bottom of the cell by filtration. The analytical data are in good agreement with the expected values.

The values of the electrochemical efficiencies, defined as the amount of metal dissolved per Faraday of charge, were close to $0.5 \text{ mol} \cdot \text{F}^{-1}$ independent of the presence or absence of additional ligands. This fact, along with the evolution of hydrogen at the cathode, is compatible with the following mechanism:

Cathode: $2HL + 2 e^- \rightarrow 2L^- + H_2$ Anode: $Cd + 2L^- \rightarrow [CdL_2] + 2 e^$ or $Cd + 2L^- + L' \rightarrow [CdL_2L'] + 2 e^-$ HL = N-2-pyridyl-sulfonamides, and L^- its deprotonation product. L' = bipy or phen

2.1 X-ray Structural Studies

Table 1 lists crystal data, experimental details, refinement results and details of structure determination.

Molecular Structure of HMs6mepy (1)

Figure 1 shows a view of the compound together with the atomic numbering scheme. Selected bond lengths and angles, along with the estimated deviations, are listed in Table 2.



Figure 1 Molecular structure of HMs6mepy.

The asymmetric unit contains two molecules connected by hydrogen bonds. The positions of the hydrogen atoms at distances of only 0.83(2) and 0.91(2) Å from the heterocyclic nitrogen, and the short values of C(15)-N(12) and C(25)-N(22) [1.347(2) and 1.343(2) Å, respectively] are consistent with an imide (I) tautomer (see Scheme 5) similar to those found in other N-2-pyridinyl benzenesulfonamide derivatives [9].

| Compound | НМѕбтеру | [Cd(Ms6mepy) ₂ (H ₂ O) ₂]H ₂ C | [Cd(Ts6mepy)2bipy] | [Cd(Ts3mepy)2bipy] | [Cd(Ms3mepy)2bipy] |
|-----------------------------------|---|---|--|---|--|
| Empirical formula | $C_{30}\;H_{36}N_4O_4S_2$ | C ₃₀ H ₄₀ N ₄ O ₇ S Cd | $C_{72} \; H_{68} \; N_{12} \; O_8 C d_2 \; S_4$ | C ₃₆ H ₃₄ N ₆ O ₄ S ₂ Cd | C40 H38N6 O4 S2 Cd |
| Formula weight | 580.75 | 745.18 | 1582.42 | 791.21 | 843.28 |
| Temperature | 293(2) K | 293(2) K | 293(2) K | 293(2) K | 293(2) K |
| Wavelength | 0.71073 A | 0.71073 A | 0.71073 A | 0.71073 A | 0.71073 A |
| Crystal system | monoclinic | monoclinic | monoclinic | orthorhombic | triclinic |
| Space group | $P2_1/n$ | <i>P</i> 2 ₁ /n | <i>P</i> 2 ₁ /c | Pna2 ₁ | P1 |
| Unit cell dimensions | a = 8.8059(5) A | a = 16.0586(16) A | a = 23.3060(14) A | a = 11.5776(14) A | $a = 9.589(4) A_{\circ}$ |
| | b = 21.9898(13) A | b = 9.6095(10) A | $b = 15.4425(9) A_{a}$ | b = 19.285(2) A | b = 13.843(5) A |
| | c = 15.3219(9) Å | c = 22.146(2) Å | c = 19.5460(12) Å | c = 17.005(2) Å | c = 16.456(7) Å |
| | | | | | $\alpha = 79.750(10)^{\circ}$. |
| | $\beta = 94.3260(10)^{\circ}$ | $\beta = 102.795(2)^{\circ}.$ | $\beta = 91.5570(10)^{\circ}.$ | | $\beta = 79.621(9)^{\circ}.$ |
| | | | | | $\gamma = 86.453(11)^{\circ}$. |
| Volume | 2958.5(3) Å ³ | 3332.6(6) Å ³ | 7032.1(7) Å ³ | 3796.7(8) Å ³ | 2113.3(15) Å ³ |
| Z | 4 | 4 | 4 | 4 | 2 |
| Density (calculated) | 1.304 Mg/m ³ | 1.485 Mg/m ³ | 1.495 Mg/m ³ | 1.384 Mg/m ³ | 1.325 Mg/m ³ |
| Absorption coefficient | 0.222 mm^{-1} | 0.831 mm^{-1} | 0.788 mm^{-1} | 0.730 mm^{-1} | 0.660 mm^{-1} |
| F(000) | 1232 | 1536 | 3232 | 1616 | 864 |
| Crystal size | $0.27 \times 0.49 \times 0.63 \text{ mm}^3$ | $0.24 \times 0.36 \times 0.66 \text{ mm}^3$ | $0.25 \times 0.27 \times 0.69 \text{ mm}^3$ | $0.18 \times 0.18 \times 0.30 \text{ mm}^3$ | $0.08 \times 0.20 \times 0.23 \text{ mm}^3$ |
| Theta range for data collection | 1.62 to 28.02° | 1.43 to 28.04°. | 1.58 to 28.02°. | 1.60 to 28.06°. | 1.28 to 28.13°. |
| Index ranges | $-10 \le h \le 11,$ | $-21 \le h \le 18$ | $-24 \le h \le 30$ | $-8 \le h \le 15$ | $-12 \le h \le 12,$ |
| | $-29 \le k \le 28,$ | $-12 \le k \le 11$ | $-20 \le k \le 19$ | $-24 \le k \le 25$ | $-18 \le k \le 10$ |
| | $-16 \le 1 \le 20$ | $-28 \le 1 \le 29$ | $-25 \le 1 \le 24$ | $-22 \le l \le 22$ | $-20 \le 1 \le 21$ |
| Reflections collected | 17649 | 19339 | 39101 | 21881 | 10864 |
| Independent reflections | 6868 [R(int) = 0.0330] | 7676 [R(int) = 0.0512] | 15532 [R(int) = 0.0378] | 8578 [R(int) = 0.0758] | 7761 [R(int) = 0.2051] |
| Completeness to theta | theta = 28.02° : 95.8 % | theta = 28.04° : 95.1 % | theta = 28.02° : 91.2% | theta = 28.06° : 98.3 % | theta = 28.13° : 75.1 % |
| Absorption correction | | Empirical | Empirical | Empirical | Empirical |
| Max. and min. Transmission | | 1.000 and 0.488 | 1.000 and 0.847 | 1.000 and 0.582 | 1.000 and 0.322 |
| Data / restraints / parameters | 6868 / 0 / 417 | 7676 / 4 / 421 | 15532 / 0 / 891 | 8578 / 1 / 446 | 7761 / 0 / 486 |
| Goodness-of-fit on F ² | 0.933 | 1.016 | 0.909 | 0.870 | 0.724 |
| Final R indices [I>2sigma(I)] | $R_1 = 0.0457, wR_2 = 0.0997$ | $R_1 = 0.0613, wR_2 = 0.1494$ | $R_1 = 0.0395, wR_2 = 0.0816$ | $R_1 = 0.0586, wR_2 = 0.1102$ | $R_1 = 0.0853, wR_2 = 0.1995$ |
| R indices (all data) | $R_1 = 0.0956, wR_2 = 0.1129$ | $R_1 = 0.1178, wR_2 = 0.1659$ | $R_1 = 0.0792, wR_2 = 0.0912$ | $R_1 = 0.1163, wR_2 = 0.1244$ | $R_1 = 0.2811, wR_2 = 0.2551$ |
| Absolute structure parameter [28 | 3] | | ā. | 0.00(3) | |
| Largest diff. peak and hole | $0.250 \text{ and } -0.275 \text{ e.}\text{\AA}^{-3}$ | 0.938 and $-0.724 \text{ e.\AA}^{-3}$ | 0.791 and $-0.465 \text{ e.}\text{\AA}^{-3}$ | 1.704 and $-0.559 \text{ e.}\text{\AA}^{-3}$ | 0.861 and $-0.725 \text{ e.}\text{\AA}^{-3}$ |

Table 1 Crystal data and structure refinement

Table 2 Selected bond lengths/Å and angles/° for HMs6mepy.

| S(1)-O(11) | 1.4371(16) | S(2)-O(21) | 1.4370(14) |
|-----------------------|------------|-----------------------|------------|
| S(1)-O(12) | 1.4382(16) | S(2)-O(22) | 1.4383(15) |
| S(1)-N(12) | 1.6034(16) | S(2)-N(22) | 1.6091(15) |
| S(1) - C(17) | 1.790(2) | S(2) - C(27) | 1.783(2) |
| N(11) - C(11) | 1.362(2) | N(21) - C(21) | 1.363(2) |
| N(11) - C(15) | 1.367(2) | N(21)-C(25) | 1.366(2) |
| N(11) - H(1) | 0.83(2) | N(21) - H(2) | 0.91(2) |
| N(12)-C(15) | 1.347(2) | N(22)-C(25) | 1.343(2) |
| C(11) - C(12) | 1.364(3) | C(21) - C(22) | 1.356(3) |
| C(11) - C(16) | 1.490(3) | C(21) - C(26) | 1.495(3) |
| C(12)-C(13) | 1.388(3) | C(22)-C(23) | 1.383(3) |
| O(11) - S(1) - O(12) | 116.25(10) | O(21) - S(2) - O(22) | 116.40(9) |
| O(11) - S(1) - N(12) | 111.78(9) | O(21) - S(2) - N(22) | 104.39(8) |
| O(12) - S(1) - N(12) | 105.48(9) | O(22) - S(2) - N(22) | 110.53(9) |
| O(11) - S(1) - C(17) | 108.71(10) | O(21) - S(2) - C(27) | 107.72(9) |
| O(12) - S(1) - C(17) | 106.26(10) | O(22) - S(2) - C(27) | 109.26(9) |
| N(12) - S(1) - C(17) | 107.93(9) | N(22) - S(2) - C(27) | 108.18(8) |
| C(11) - N(11) - C(15) | 125.28(19) | C(21)-N(21)-C(25) | 124.78(18) |
| C(15) - N(12) - S(1) | 120.56(14) | C(25) - N(22) - S(2) | 121.77(14) |
| N(11)-C(11)-C(12) | 117.9(2) | C(22) - C(21) - N(21) | 118.1(2) |
| N(11) - C(11) - C(16) | 117.42(19) | C(22) - C(21) - C(26) | 124.97(19) |
| C(12) - C(11) - C(16) | 124.66(19) | N(21) - C(21) - C(26) | 116.96(19) |

Hydrogen bond parameters /Ű for HMs6mepy.

| D-H···A | d(D-H) | d(H···A) | $d(D{\cdots}A)$ | <(DHA) |
|-----------------------------------|---------|----------|-----------------|-----------|
| N(11)-H(1)N(22) | 0.83(2) | 2.15(2) | 2.975(2) | 174.4(19) |
| N(21) - H(2) - N(12) | 0.91(2) | 2.11(2) | 3.004(2) | 167.8(19) |
| C(113) - H(11B) - O(11) | 0.96 | 2.37 | 2.708(3) | 100.1 |
| C(14)-H(14)O(11) | 0.95(2) | 2.52(2) | 3.069(3) | 116.8(16) |
| C(215) - H(21G) - N(22) | 0.96 | 2.63 | 3.066(3) | 108.1 |
| C(215)-H(21H)O(21) | 0.96 | 2.45 | 3.097(3) | 124.7 |
| $C(26) - H(26^{\circ}) - O(12)$ | 0.96 | 2.40 | 3.187(3) | 139.5 |
| $C(13) - H(13) - O(22)^{1}$ | 0.95(2) | 2.57(2) | 3.308(3) | 134.5(16) |
| C(23)-H(23)···O(21) ¹¹ | 0.92(2) | 2.49(2) | 3.350(3) | 154.4(18) |

Symmetry transformations used to generate equivalent atoms: i = x - 1/2, -y + 1/2, z - 1/211 = x + 1, y, z

In addition, the molecules of HMs6mepy are associated by intermolecular hydrogen bonds between the atoms in two independent molecules of the unit cell, leading to the formation of a dimer. These hydrogen bonds are between the pyridine nitrogen atom of one molecule and the amide nitrogen atom of the other neighbour. In addition, one oxygen atom of the sulfone group [O(22), O(12)] of one molecule is involved in a hydrogen bond with the nitrogen of the pyridine ring [N(11), N(21)] of the other, so each H(N)atom is participating in a bifurcated hydrogen bond with the N_{amide} and one oxygen atoms of the other molecule in the asymmetric unit. This situation causes a distortion of the bond angles around the sulfur atom, with values in the range of 104.39(8)-116.40(9)°.



Scheme 5

Both the phenyl and the pyridine rings are almost planar, with the largest deviations from planarity being 0.013(3) and 0.012(8) Å, respectively. The interplanar angles of $83.83(13)^{\circ}$ and $86.73(11)^{\circ}$ are similar to those found in other sulfonamides [9].

Molecular Structure of $[Cd(Ms6mepy)_2(H_2O)_2] \cdot H_2O$ (2)

The molecular structure of $[Cd(Ms6mepy)_2(H_2O)_2]\cdot H_2O$ is shown in Figure 2, together with the atomic numbering scheme adopted. Selected bond distances and angles are listed in Table 3.

Table 3 Selected bond lengths/Å and angles/° for $[Cd(Ms6mepy)_2(H_2O)_2] H_2O$

| Cd-O(1W) | 2.316(5) | Cd-N(12) | 2.318(4) |
|----------------------|------------|-----------------------|------------|
| Cd-N(22) | 2.320(4) | Cd-O(2W) | 2.325(6) |
| Cd-N(21) | 2.333(4) | Cd-N(11) | 2.351(4) |
| S(1) - O(12) | 1.418(4) | S(1) - O(11) | 1.441(4) |
| S(1) - N(12) | 1.583(4) | S(1) - C(17) | 1.779(6) |
| S(2) - O(21) | 1.440(4) | S(2)-O(22) | 1.459(4) |
| S(2) - N(22) | 1.590(5) | S(2) - C(27) | 1.791(5) |
| N(11) - C(15) | 1.337(6) | N(11) - C(11) | 1.341(7) |
| N(12) - C(15) | 1.384(6) | N(21)-C(25) | 1.335(7) |
| N(21) - C(21) | 1.346(7) | N(22)-C(25) | 1.384(6) |
| | | | |
| O(1W)-Cd-N(12) | 110.44(18) | O(1W)-Cd-N(22) | 88.96(18) |
| N(12)-Cd-N(22) | 152.61(15) | O(1W)-Cd-O(2W) | 82.9(3) |
| N(12)-Cd-O(2W) | 93.6(2) | N(22)-Cd-O(2W) | 108.3(2) |
| O(1W) - Cd - N(21) | 144.45(19) | N(12)-Cd-N(21) | 105.05(16) |
| N(22)-Cd-N(21) | 57.14(16) | O(2W)-Cd-N(21) | 97.0(2) |
| O(1W) - Cd - N(11) | 93.57(18) | N(12) - Cd - N(11) | 57.28(15) |
| N(22) - Cd - N(11) | 103.94(15) | O(2W) - Cd - N(11) | 147.4(2) |
| N(21) - Cd - N(11) | 104.06(14) | O(12) - S(1) - O(11) | 115.5(3) |
| O(12) - S(1) - N(12) | 112.6(3) | O(11) - S(1) - N(12) | 105.3(2) |
| O(12) - S(1) - C(17) | 107.7(2) | O(11) - S(1) - C(17) | 107.5(3) |
| N(12) - S(1) - C(17) | 108.0(2) | O(21) - S(2) - O(22) | 115.8(3) |
| O(21) - S(2) - N(22) | 112.1(3) | O(22) - S(2) - N(22) | 104.7(2) |
| O(21) - S(2) - C(27) | 108.7(3) | O(22) - S(2) - C(27) | 107.7(3) |
| N(22) - S(2) - C(27) | 107.4(2) | C(15) - N(11) - C(11) | 120.8(5) |
| | . / | | ~ / |

Hydrogen bonds parameters /Å,° for [Cd(Ms6mepy)₂(H₂O)₂]H₂O

| D-H···A | $d(D\!-\!H)$ | d(H…A) | $d(D{\cdots}A)$ | <(DHA) |
|---------------------|--------------|---------|-----------------|--------|
| O(1W)-H(1A)···O(22) | 0.83(2) | 2.19(5) | 2.907(7) | 146(7) |
| O(2W)-H(2B)···O(11) | 0.83(2) | 2.59(6) | 3.161(9) | 128(7) |
| O(2W)-H(2°)···O(3W) | 0.82(2) | 2.48(5) | 3.061(11) | 129(6) |
| O(1W)-H(1B)···O(3W) | 0.80(2) | 2.12(5) | 2.781(8) | 141(7) |



Figure 2 Molecular structure of $[Cd(Ts6mepy)_2(H_2O)_2]H_2O$. The insert represents the environment around the metal atom.

The compound crystallises with a water molecule, which establishes a relationship with the molecule through hydrogen bonds. The cadmium atom is coordinated by two anionic (N,N')-bidentate sulfonamide ligands and by two water molecules. In this arrangement the metal atom is hexacoordinated in an environment that is best described as a distorted trigonal prism. The triangular faces of the prism are formed by a sulfonamide nitrogen atom, a pyridine nitrogen atom of a different ligand and by a water molecule, with the sulfonamide ligands situated at the edge of the parallelogram faces in an alternating fashion. The angles ϕ (see scheme 6) [13], have values of -23.4(2), -29.2(2) and $-27.6(3)^{\circ}$.



Scheme 6

The triangular faces form a dihedral angle of $20.0(1)^{\circ}$ as a consequence of the small bite of the bidentate ligands. This is the main source of distortion, with angles N_{pv}-Cd-N_{sulfonamide} of 57.28(15) and 57.14(16)°, respectively. This angle is not very different from those found in similar complexes that have been reported previously [10, 14]. The Cd-N_{amide} bond distances, 2.318(4) and 2.320(4) Å, are similar to those described in the aforementioned references slightly longer than those and are found in K[Cd(ClC₆H₄SO₂NCONH-n-Pr)₃][15] and in [Cd(bipy)₂-(bsglyNO)₂] [16] with mean Cd-N_{amide} distances of 2.21(2) and 2.215 Å, respectively. The two $Cd-N_{pv}$ bond distances are 2.333(4) and 2.351(4) Å, which are similar to those found in other hexacoordinated cadmium complexes (2.310-2.346 Å) [17, 18].

The Cd- O_w bond lengths are 2.316(5) and 2.325(6) Å and are not very different to those found in other diaquocomplexes of hexacoordinated cadmium(II) [see for example catena-{hexakis[μ^2 -1,3-bis(4-pyridyl)propane]-bis(μ^2 sulfato-O,O',O'')-hexa-aqua-bis(hydrogensulfato-O)-tetracadmium nonahydrate} [19], catena-[bis(μ^2 -4,4'-bipyridyl)diaqua-cadmium(II) dinitrate tetrahydrate] [20] or [10,16-dioxa-3,13,23,29-tetra-azatetracyclo(23.3.1.0^{4,9}.0^{17,22})nonacosa-(29),2,4(9)5,7,17,19,21,23,25,27-undecaene]-diaguacadmium(II) diperchlorate [21]. The coordinated water molecules are implicated in two intramolecular hydrogen bonds, one involves the SO₂ group of one of the ligands and the other involves the water of crystallization (see Table 5). This water molecule is undoubtedly implicated in some hydrogen bonds with the SO₂ groups and the supramolecular structure should probably be maintained through hydrogen bonds. Unfortunately, the quality of the data does not allow location of the hydrogen atoms.

The dihedral angles between the benzene and pyridine rings are 83.6(2) and $74.4(2)^{\circ}$ for the two ligands, respec-

tively, and these values are slightly different to those found in the free ligand [9] due to the effect of the coordination.

The two pyridine rings coordinated to the metal atom are almost perpendicular to one another and form a dihedral angle of $87.7(2)^{\circ}$. These rings are planar to within 0.015(5)Å and the cadmium atoms are 0.204(7) and 0.274(8)Å out of the best planes, respectively, as a consequence of the constraint caused by the bidentate character of the ligands.

| | | 0 | | | | | |
|---------|------|-----------|-------|----------|-----|------------|----------|
| Table 4 | Bond | lengths/A | and a | ngles/° | for | [Cd(Ts6mep | y),bipy] |
| | | <u> </u> | | <u> </u> | | L \ | |

| | 2 200(2) | | 2.244(2) |
|-----------------------|------------|-----------------------|------------|
| Cd(1) = N(12) | 2.299(2) | Cd(1) = N(31) | 2.344(3) |
| Cd(1) = N(32) | 2.345(3) | Cd(1) = N(22) | 2.358(2) |
| Cd(1) = N(21) | 2.387(2) | Cd(1) = N(11) | 2.427(3) |
| S(1) = O(11) | 1.434(3) | S(1) = O(12) | 1.436(3) |
| S(1) - N(12) | 1.594(3) | S(1) - C(17) | 1.770(3) |
| N(12) - C(15) | 1.378(4) | N(11) - C(11) | 1.346(4) |
| N(11) - C(15) | 1.360(4) | S(2) - O(21) | 1.434(2) |
| S(2) - O(22) | 1.448(2) | S(2) - N(22) | 1.584(3) |
| S(2) - C(27) | 1.772(3) | N(21)-C(21) | 1.342(4) |
| N(21) - C(25) | 1.349(4) | N(22)-C(25) | 1.388(4) |
| Cd(2) - N(51) | 2.305(3) | Cd(2) - N(61) | 2.338(2) |
| Cd(2) - N(42) | 2.339(2) | Cd(2) - N(62) | 2.339(2) |
| Cd(2) - N(41) | 2.373(2) | Cd(2)-N(52) | 2.486(3) |
| S(4)-O(42) | 1.439(2) | S(4) - O(41) | 1.442(2) |
| S(4) - N(42) | 1.593(2) | S(4) - C(47) | 1.765(3) |
| N(41)-C(41) | 1.345(4) | N(41)-C(45) | 1.353(3) |
| N(42)-C(45) | 1.373(4) | S(5)-O(51) | 1.437(3) |
| S(5)-O(52) | 1.445(3) | S(5)-N(52) | 1.592(3) |
| S(5)-C(57) | 1.776(4) | N(51)-C(51) | 1.350(4) |
| N(51)-C(55) | 1.361(4) | N(52)-C(55) | 1.371(4) |
| N(12)-Cd(1)-N(31) | 99.61(9) | N(12)-Cd(1)-N(32) | 155.37(9) |
| N(31)-Cd(1)-N(32) | 70.51(9) | N(12)-Cd(1)-N(22) | 107.41(8) |
| N(31)-Cd(1)-N(22) | 143.77(9) | N(32)-Cd(1)-N(22) | 92.05(9) |
| N(12)-Cd(1)-N(21) | 102.23(9) | N(31)-Cd(1)-N(21) | 94.75(9) |
| N(32)-Cd(1)-N(21) | 101.08(8) | N(22)-Cd(1)-N(21) | 56.61(9) |
| N(12)-Cd(1)-N(11) | 56.64(8) | N(31) - Cd(1) - N(11) | 117.70(8) |
| N(32)-Cd(1)-N(11) | 106.94(8) | N(22)-Cd(1)-N(11) | 97.45(8) |
| N(21) - Cd(1) - N(11) | 142.50(8) | O(11) - S(1) - O(12) | 118.06(17) |
| O(11) - S(1) - N(12) | 112.38(15) | O(12) - S(1) - N(12) | 105.48(14) |
| O(11) - S(1) - C(17) | 106.75(16) | O(12) - S(1) - C(17) | 106.25(16) |
| O(21) - S(2) - O(22) | 117.18(14) | O(21) - S(2) - N(22) | 105.89(14) |
| O(22) - S(2) - N(22) | 113.36(14) | O(21) - S(2) - C(27) | 106.72(15) |
| O(22) - S(2) - C(27) | 106.17(14) | N(22) - S(2) - C(27) | 106.93(14) |
| N(51) - Cd(2) - N(61) | 115.14(9) | N(51) - Cd(2) - N(42) | 99.55(8) |
| N(61) - Cd(2) - N(42) | 145.06(9) | N(51) - Cd(2) - N(62) | 112.32(10) |
| N(61) - Cd(2) - N(62) | 70.23(9) | N(42) - Cd(2) - N(62) | 93.59(9) |
| N(51) - Cd(2) - N(41) | 137.47(9) | N(61) - Cd(2) - N(41) | 96.45(8) |
| N(42) - Cd(2) - N(41) | 56.73(8) | N(62) - Cd(2) - N(41) | 104.56(9) |
| N(51) - Cd(2) - N(52) | 55 71(10) | N(61) - Cd(2) - N(52) | 93 90(9) |
| N(42) - Cd(2) - N(52) | 109.81(8) | N(62) - Cd(2) - N(52) | 154 71(9) |
| N(41) - Cd(2) - N(52) | 96 51(9) | O(42) - S(4) - O(41) | 116 22(14) |
| O(42) = S(4) = N(42) | 106 20(13) | O(41) - S(4) - N(42) | 113 15(13) |
| O(42) - S(4) - C(47) | 106 66(14) | O(41) - S(4) - C(47) | 106 63(13) |
| N(42) - S(4) - C(47) | 107 52(13) | O(51) - S(5) - O(52) | 116 13(17) |
| O(51) - S(5) - N(52) | 106.09(15) | O(52) - S(5) - N(52) | 113 22(17) |
| O(51) - S(5) - C(57) | 107 52(18) | O(52) - S(5) - C(57) | 106 65(17) |
| N(52) - S(5) - C(57) | 106 75(15) | 0(02) 0(0) 0(0) | 100.00(17) |
| | | | |

| | | | - | | | | | | |
|----------|---------|-------------|-----|-------|------|-------|------------------|-----|----|
| Hydrogen | bonds 1 | parameters. | /Α, | ° for | [Cd(| Ts6me | py) ₂ | bip | y] |

| D-H···A | d(D-H) | d(H···A) | d(D…A) | <(DHA) |
|------------------------------------|--------|----------|----------|--------|
| C(14)-H(14)O(11) | 0.93 | 2.48 | 3.017(5) | 117.1 |
| C(24) - H(24) - O(22) | 0.93 | 2.46 | 3.021(4) | 119.2 |
| $C(38) - H(38) - O(52^{i})$ | 0.93 | 2.49 | 3.273(4) | 142.0 |
| C(44) - H(44) - O(41) | 0.93 | 2.50 | 3.046(4) | 117.5 |
| $C(46) - H(46B) \cdots O(12^{ii})$ | 0.96 | 2.58 | 3.432(4) | 148.3 |
| C(54)-H(54)O(52) | 0.93 | 2.40 | 2.983(5) | 120.8 |
| C(56)-H(56A)O(42) | 0.96 | 2.35 | 3.263(5) | 159.5 |
| C(112) - H(112) - O(11) | 0.93 | 2.53 | 2.909(4) | 104.7 |
| C(212)-H(212)O(22) | 0.93 | 2.55 | 2.914(4) | 103.8 |
| $C(411) - H(411) - O(11^{iii})$ | 0.93 | 2.58 | 3.201(4) | 124.9 |
| C(412)-H(412)····O(41) | 0.93 | 2.54 | 2.910(4) | 103.9 |
| C(512)-H(512)···O(52) | 0.93 | 2.55 | 2.917(5) | 104.2 |

Symmetry transformations used to generate equivalent atoms: $^{i}-x+1$, y-0.5, 0.5-z; ^{ii}x , y+1, z; $^{iii}2$ -x, y+0.5, 0.5-z.

Molecular Structure of $[Cd(Ts6mepy)_2 bipy]$ (3)

The asymmetric unit contains two independent molecules of the compound. For the sake of clarity Figure 3 shows only one of these molecules, together with the atomic numbering scheme adopted. Selected bond distances and angles are listed in Table 4.



Figure 3 Molecular structure of [Cd(Ts6mepy)₂bipy]. The insert represents the environment around the metal atom.

The two independent molecules of the compound are chemically identical. In both molecules the cadmium atom is coordinated by the two nitrogen atoms of two monoanionic (N,N')-bidentate ligands and by two nitrogen atoms of the 2,2'-bipyridine coligand. The torsion angle ϕ has an average value of 22.3(1)°. Therefore, the coordination polyhedron around the cadmium atom is best described as a distorted trigonal prism, with the (N,N)-donor atoms of each ligand defining two of the edges of the parallelogram-shaped faces of the prism. The nitrogen atoms of the 2,2'-bipyridine form the other edge. The triangular faces of the prism are formed by one of the 2,2'-bipyridine nitrogen atoms and the N_{amide} and N_{py} atoms of each ligand. These triangular faces are not parallel but have a dihedral angle of 8.2(1) or $5.3(2)^{\circ}$ for each molecule due to the small bite of the anionic ligand [N-Cd-N 56.61(9)], 56.64(8), 55.71(10) and 56.73(8)°]. The N-Cd-N angles of the neutral ligands, 70.23(9) and 70.51(9)°, are similar to those reported for hexacoordinated cadmium complexes containing coordinated 2,2'-bipyridine.

The benzene and pyridine rings of the anionic ligands adopt an almost perpendicular disposition, with dihedral angles of 81.3(1), 82.5(1), 86.5(1) and $89.7(1)^\circ$. These angles are very similar to those found in the free ligand. The coordinated pyridine rings also adopt a perpendicular disposition, with dihedral angles of 88.5(1) and $89.7(1)^\circ$ with respect to each other when coordinated to the same metal atom. The cadmium atom is 0.485(4), 0.298(4), 0.427(4) and 0.377(5) Å out of the best plane defined by each pyridine ring.

The two planar pyridine rings of the coordinated bipyridine ligands form dihedral angles of 8.5(2) and $8.8(1)^{\circ}$. The Cd1 atom is 0.118(5) and 0.509(5) Å out of the best plane of these rings and the Cd2 atom is 0.203(5) and 0.590(5) Å out of the best planes.

It is worth noting that the coordination mode of this ligand, i.e. an (N,N')-donor, is similar to that described previously by our group [10] for a complex without a substituent on the pyridine ring but is different to those described in this paper (vide infra).

Molecular Structure of $[Cd(Ts3mepy)_2bipy]$ (4)

The molecular structure of $[Cd(Ts3mepy)_2bipy]$ is shown in Figure 4, together with the atomic numbering scheme adopted. Selected bond distances and angles are listed in Table 5.

 Table 5
 Selected bond lengths/Å and angles/° for [Cd(Ts3mepy)2

 bipy]

| Cd-O(21) | 2.272(4) | Cd-O(11) | 2.305(5) |
|----------------------|------------|----------------------|------------|
| Cd - N(21) | 2.316(5) | Cd - N(11) | 2.320(6) |
| Cd-N(31) | 2.352(5) | Cd - N(32) | 2.369(6) |
| S(1) - O(12) | 1.440(5) | S(1) = O(11) | 1.465(5) |
| S(1) - N(12) | 1.572(6) | S(1) - C(17) | 1.764(7) |
| S(2) - O(22) | 1.420(5) | S(2) - O(21) | 1.486(5) |
| S(2) - N(22) | 1.555(7) | S(2) - C(27) | 1.762(8) |
| N(11)-C(15) | 1.353(8) | N(11)-C(11) | 1.361(9) |
| N(12)-C(15) | 1.368(8) | N(21)-C(21) | 1.318(10) |
| N(21)-C(25) | 1.352(9) | N(22)-C(25) | 1.354(10) |
| O(21)-Cd-O(11) | 97.27(19) | O(21)-Cd-N(21) | 82.91(19) |
| O(11) - Cd - N(21) | 87.86(19) | O(21) - Cd - N(11) | 85.28(18) |
| O(11) - Cd - N(11) | 82.9(2) | N(21) - Cd - N(11) | 164.0(2) |
| O(21)-Cd-N(31) | 164.17(19) | O(11)-Cd-N(31) | 98.08(19) |
| N(21)-Cd-N(31) | 93.8(2) | N(11)-Cd-N(31) | 100.43(19) |
| O(21)-Cd-N(32) | 94.9(2) | O(11)-Cd-N(32) | 167.19(18) |
| N(21)-Cd-N(32) | 97.7(2) | N(11)-Cd-N(32) | 94.0(2) |
| N(31)-Cd-N(32) | 70.1(2) | O(12) - S(1) - O(11) | 113.5(3) |
| O(12) - S(1) - N(12) | 108.1(3) | O(11)-S(1)-N(12) | 114.3(3) |
| O(22)-S(2)-O(21) | 113.4(3) | O(22)-S(2)-N(22) | 108.0(4) |
| O(21) - S(2) - N(22) | 114.6(3) | O(22) - S(2) - C(27) | 108.6(3) |
| O(21)-S(2)-C(27) | 103.9(3) | N(22)-S(2)-C(27) | 108.0(4) |
| | | | |

Hydrogen bonds parameters /Å,° for [Cd(Ts3mepy)2bipy].

| D-H···A | d(D-H) | $d(H \cdots A)$ | $d(D \cdots A)$ | <(DHA) |
|------------------------------------|--------|-----------------|-----------------|--------|
| $C(12) - H(12) - O(12^{i})$ | 0.93 | 2.55 | 3.406(9) | 153.8 |
| C(28)-H(28)O(21) | 0.93 | 2.57 | 2.905(11) | 101.9 |
| C(34)-H(34)N(12ii) | 0.93 | 2.44 | 3.348(9) | 165.5 |
| C(37)-H(37)···N(12 ⁱⁱ) | 0.93 | 2.48 | 3.363(10) | 158.2 |
| C(112)-H(112)···O(11) | 0.93 | 2.56 | 2.927(9) | 103.6 |

Symmetry transformations used to generate equivalent atoms:

ⁱ 2-x, 1-y, z+0.5 ⁱⁱ x-0.5, 0.5-y, z.

The central cadmium atom is six-coordinated, but there are two important differences in comparison to the complex $[Cd(Ts6mepy)_2bipy]$. Firstly, the anionic ligands behave in an (N,O) bidentate way, using one of the oxygen atoms of the sulfonyl groups and the nitrogen atom of the pyridine ring. The second difference concerns the coordination polyhedron. In this case, the arrangement is closer to an octahedron as the torsion angles ϕ now have values of 30.6(2), 49.4(2) and 49.0(2)°, which are not far removed from the expected values for an ideal octahedron (45°).



Figure 4 Molecular structure of [Cd(Ts3mepy)₂bipy]. The insert represents the environment around the metal atom.

The cadmium atom is coordinated by two (N,O)-bidentate anionic ligands and an (N,N')-bidentate 2,2'-bipyridine molecule. The arrangement of the two ligands is such that the two oxygen atoms are in *cis* positions and the two pyridine nitrogen are trans with respect to each other. These positions can be defined as the axial positions. The cadmium atom is only 0.002(2) Å out of the best equatorial plane (rms of 0.0906). The two pyridine rings of the bipyridine moiety are planar within 0.006 Å, with a dihedral angle between them of $5.5(4)^{\circ}$, and are almost coplanar with the best equatorial plane [dihedral angles of 7.3(3) and $7.8(3)^{\circ}$]. One of the sources of distortion of the polyhedron is the small bite of the bipyridine ligand $[70.1(2)^{\circ}]$, which forms a 5-membered chelate ring. All the other angles around the cadmium atom are close to 90°. The Cd-N bond distances are similar to those found in other complexes containing this ligand [10] and the Cd-O bond distances are slightly different, probably due to packing effects. These bond lengths are shorter than those found in other cadmium(II) complexes with this kind of bond [10, 22]. The benzene ring and the pyridine ring of each anionic ligand, which are almost perpendicular in the free ligand, form dihedral angles of 77.3(3) and 57.9(3)° as a result of coordination. The pyridine rings of the anionic ligands form a dihedral angle of 88.3(2) and 88.0(2)° with the equatorial plane, but they are not parallel to each other [dihedral angle of 17.6(3)°].

Molecular Structure of [Cd(Ms3mepy)₂bipy] (5)

Unfortunately, the crystal data for the complex $[Cd(Ms3mepy)_2bipy]$ are of poor quality. Nevertheless, the refinement gives the final map shown in Figure 5 and the final R₁ converged to 8.5 %. Several attempts to crystallize

a better quality monocrystal were unsuccessful. Selected bond distances and angles are listed in Table 6.

Table 6 Selected bond lengths/Å and angles/° for [Cd(Ms3mepy)₂₋ bipy]

| Cd-N(21) | 2.293(12) | Cd-N(11) | 2.310(12) |
|-----------------------|-----------|-----------------------|-----------|
| Cd - N(31) | 2.347(13) | Cd - O(22) | 2.359(8) |
| Cd - O(11) | 2.365(9) | Cd - N(32) | 2.388(11) |
| S(11)-O(12) | 1.479(9) | S(11) - O(11) | 1.480(9) |
| S(11) - N(12) | 1.572(12) | S(11) - C(17) | 1.776(14) |
| S(21)-O(21) | 1.464(9) | S(21)-O(22) | 1.467(9) |
| S(21)-N(22) | 1.616(13) | S(21) - C(27) | 1.755(13) |
| N(11)-C(15) | 1.336(16) | N(11)-C(11) | 1.384(16) |
| N(12)-C(15) | 1.387(16) | N(21)-C(25) | 1.351(15) |
| N(21)-C(21) | 1.364(17) | N(22)-C(25) | 1.344(17) |
| | | | |
| N(21)-Cd-N(11) | 145.9(4) | N(21)-Cd-N(31) | 119.2(4) |
| N(11)-Cd-N(31) | 89.6(5) | N(21)-Cd-O(22) | 78.4(4) |
| N(11)-Cd-O(22) | 83.8(4) | N(31)-Cd-O(22) | 90.8(4) |
| N(21)-Cd-O(11) | 82.2(4) | N(11)-Cd-O(11) | 79.0(4) |
| N(31)-Cd-O(11) | 150.6(4) | O(22)-Cd-O(11) | 114.4(3) |
| N(21)-Cd-N(32) | 98.3(4) | N(11)-Cd-N(32) | 109.5(4) |
| N(31) - Cd - N(32) | 69.2(4) | O(22) - Cd - N(32) | 155.2(3) |
| O(11) - Cd - N(32) | 89.1(4) | O(12) - S(11) - O(11) | 113.7(6) |
| O(12) - S(11) - N(12) | 104.7(7) | O(11) - S(11) - N(12) | 114.3(6) |
| O(12) - S(11) - C(17) | 107.7(6) | O(11) - S(11) - C(17) | 106.8(7) |
| N(12)-S(11)-C(17) | 109.3(7) | O(21)-S(21)-O(22) | 112.7(7) |
| O(21)-S(21)-N(22) | 105.8(7) | O(22) - S(21) - N(22) | 113.1(6) |
| O(21)-S(21)-C(27) | 107.0(7) | O(22)-S(21)-C(27) | 107.2(7) |
| N(22)-S(21)-C(27) | 110.9(7) | | |
| | | | |

Hydrogen bonds parameters /Å,° for for [Cd(Ms3mepy)₂bipy]

| D-H···A | d(D-H) | $d(H{\cdots}A)$ | d(D…A) | <(DHA) |
|----------------------------------|--------|-----------------|-----------|--------|
| C(11)-H(11)···O(22) | 0.93 | 2.50 | 3.061(18) | 118.8 |
| C(113)-H(11D)···O(12) | 0.96 | 2.43 | 2.828(19) | 104.4 |
| C(21)-H(21)···O(11) | 0.93 | 2.34 | 2.96(2) | 124.4 |
| C(213)-H(21A)···O(22) | 0.96 | 2.42 | 2.761(18) | 100.5 |
| C(215)-H(21I)O(21) | 0.96 | 2.22 | 2.718(18) | 111.1 |
| C(310)-H(310)···O(12) | 0.93 | 2.53 | 3.038(18) | 114.6 |
| $C(34) - H(34) \cdots N(12^{i})$ | 0.93 | 2.48 | 3.385(19) | 163.7 |
| C(39)-H(39)O(12 ⁱⁱ) | 0.93 | 2.51 | 3.262(18) | 138.0 |
| | | | | |

Symmetry transformations used to generate equivalent atoms: ⁱ 2-x, 1-y, 1-z, ⁱⁱ 1-x, 1-y, 1-z



Figure 5 Molecular structure of [Cd(Ms3mepy)₂bipy]. The insert represents the environment around the metal atom.

The cadmium atom is six-coordinated by two anionic sulfonamide ligands that act as (N,O) donors and by a 2,2'-bipyridine molecule acting in an (N,N') chelating manner.

The average value of ϕ is 24.3(5)°, so the coordination polyhedron around the cadmium atom can be described as a distorted trigonal prism. The triangular faces of the prism are formed by three different donor atoms and these form a dihedral angle of $7.4(6)^{\circ}$. The three chelating ligands are in the vertical edges of the prism.

Once again it is worth noting the coordination mode of the ligand, which employs one of the oxygen atoms of the sulfone groups for coordination to the cadmium atom. The other donor atom is the pyridine nitrogen atom and, consequently, the sulfonamide nitrogen atoms are not implicated in the coordination, a situation similar to that in the previous complex but different to those described in the literature [10].

2.2 Spectroscopic studies

The IR spectra of the complexes do not show the band attributable to v(N-H), which in the free ligands appears at 3248-3222 cm⁻¹, thus confirming that the hydrogen atom of the amide group is lost during the electrolysis. The bands of the ligands in the range 1590-1616 cm⁻¹, attributable to the v(C=N), appear in similar positions except in the complexes with the ligands Ts6mepy⁻ and Ms6mepy⁻, in which they are shifted to lower frequencies as a result of the coordination through the sulfonamide atom. The bands of the ligands in the range 1135-1125 cm⁻¹, attributable to the $v_{svm}(S=O)$, appear slightly shifted to lower frequencies in the spectra of complexes with Ts3mepy⁻ and Ms3mepy⁻ as a result of the coordination through the sulfonyl group.

In addition, the IR spectra of the mixed complexes show IR absorptions typical of coordinated 2,2'-bipyridine (around 765 and 735 cm^{-1}) and 1,10-phenanthroline (1520, 850 and 720 cm⁻¹).

The complexes were also studied by ¹H NMR spectroscopy but, unfortunately, the binary compounds of general formula CdL₂ are insoluble in most organic solvents. The ¹H NMR spectra of the mixed complexes do not show the peak at about 9-13 ppm, as one would expect for a deprotonated ligand. All of the other expected signals are present in the spectra. A peak at about 2.35 ppm due to the toluene methyl group for the cadmium complexes of Ts3mepy⁻ and Ts6mepy⁻, and for Ms3mepy⁻ and Ms6mepy⁻ two peaks are observed at about 2.70 and 2.25 ppm due to the mesytilene methyl groups. For Ts3mepy⁻ and Ms3mepy⁻ the pyridine methyl group gives rise to a signal close to 2.15 ppm and for Ts6mepy⁻ and Ms6mepy⁻ the pyridine methyl group appears in the range 2.20 to 2.40 ppm. Aromatic peaks, including those for the coligands, are between 6 and 8 ppm.

The mass spectra of some of the complexes could not be recorded for solubility reasons. For the other complexes the LSIMS show the molecular ion with appropriate isotope distributions. In many cases, the ions formed by loss of one ligand from the initial complex are also observed, as well as a peak attributed to the free ligand.

3 Conclusions

This paper describes a series of cadmium complexes of several sulfonamides ligands. The features of the X-ray diffraction determined structures are summarized in Table 7.

Table 7Conclusions.

| Complex | Sulfonamide ligand behaviour | Environment around the metal atom |
|--|---|--|
| [Cd(Ms6mepy) ₂ (H ₂ O) ₂] [Cd(Ts6mepy) ₂ bipy] [Cd(Ts3mepy) ₂ bipy] [Cd(Ms3mepy) ₂ bipy] | (N, N) bidentate (N, N) bidentate (N, O) bidentate (N, O) bidentate) | $\begin{array}{l} [CdN_4O_2] \\ [CdN_6] \\ [CdN_4O_2] \\ [CdN_4O_2] \end{array}$ |

As can be seen, the ligands behave in a (N, O) bidentate way when a substituent is located in position 3. However, when the substituent is in position 6, the ligands 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 proximity of the metal atom, and induces a (N, O) bidentate behaviour. It should be noted that the ligands behave in a (N, N) way when they have not substituents neither in position 3 nor in position 6 [10].

4 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, anhydrous magnesium sulfate, and all other reagents were commercial products and were used as supplied. Cadmium (Aldrich) was used as 2×2 cm plates.

Preparation of ligands

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

HMs6mepy: This ligand was synthesized by mixing 2-amino-6picoline (2 g, 18.4 mmol) and 2-mesitylenesulfonyl chloride (4.05 g, 18.4 mmol) in dichloromethane. An aqueous solution of sodium carbonate (1.95 g, 18.4 mmol in 20 mL water) was added dropwise to the above solution. The mixture was stirred overnight and water (100 mL) was added. The organic layer was dried with anhydrous magnesium sulfate, the solvent was evaporated and the resulting oil was treated with ethanol. A white solid was obtained and was identified as HMs6mePy. Anal. C. 61.3, H. 6.4, N. 9.5, S. 10.9 % Calcd. for $C_{15}N_2H_{18}O_2S$ C. 62.1, H. 6.2, N. 9.6, S. 11.0 %.

¹**H NMR** (CDCl₃, ppm) 2.37(s), 3H, CH₃(py); 2.24(s), 3H, CH₃(*p*-tolyl); 2.69(s), 6H, CH₃(*o*-tolyl); 6.55(d), 1H, py; 6.74(d), 1H, py; 6.88(s), 2H, tolyl; 7.37(d), 1H, py; 12.33(b), 1H, NH. **IR** (KBr, cm⁻¹): 3236(w), 2931(w), 1616(vs), 1533(m), 1362(vs), 1136(vs). **EI MS**: *m*/*z*: 291 (4 %, *M*⁺); 108 (13 %, *M*⁺ – {O₂S-mesityl}).

HMs3mepy: Anal. C. 61.3, H. 6.0, N. 9.3, S. 11.2 %. Calcd. for $C_{15}N_2H_{18}O_2S$ C. 62.1, H. 6.2, N. 9.6, S. 11.0 %.

¹**H NMR** (CDCl₃, ppm) 2.15(s), 3H, CH₃(py); 2.25(s), 3H, CH₃(*p*-tolyl); 2.71(s), 6H, CH₃(*o*-tolyl); 6.47(d), 1H, py; 6.89(s), 2H, tolyl; 7.36(d), 1H, py; 7.42(d), 1H, py; 12.33(b), 1H, NH. **IR** (KBr, cm⁻¹): 3222(m), 2940(w),

1595(s), 1544(s), 1338(s), 1098(s). EI MS: m/z: 291 (100 %, M^+); 108 (10 %, $M^+ - \{O_2S\text{-mesityl}\}$).

HTs6mepy: Anal. C. 58.8, H. 5.6, N. 10.6, S. 12.3 % Calcd. for $C_{13}N_2H_{14}O_2S$ C. 59.5, H. 5.4, N. 10.7, S. 12.2 %.

¹**H NMR** (CDCl₃, ppm) 2.41(s), 3H, CH₃(py); 2.36(d), 3H, CH₃(tolyl); 6.60(d), 1H, py; 7.46(dd), 1H, py; 7.06(d), 1H, py; 7.22(d), 2H, tolyl; 7.79(d), 2H, tolyl; 9.95(b), 1H, NH. **IR** (KBr, cm⁻¹): 3231(w), 2958(w), 1612(vs), 1534(m), 1369(s), 1134(s). **EI MS**: m/z: 262 (6 %, M^+); 108 (3 %, $M^+ - \{O_2S$ -tolyl}).

HTs3mepy: Anal. C. 58.7, H. 5.7, N. 10.2, S. 11.8 % Calcd. for $C_{13}N_2H_{14}O_2S$ C. 59.5, H. 5.4, N. 10.7, S. 12.2 %.

¹**H NMR** (CDCl₃, ppm) 2.15(s), 3H, CH₃(py); 2.35(d), 3H, CH₃(tolyl); 6.50(d), 1H, py; 7.40(d), 1H, py; 7.49(d), 1H, py; 7.85(d), 2H, tolyl; 7.21(d), 2H, tolyl; 12.14(b), 1H, NH. **IR** (KBr, cm⁻¹): 3248(m), 2951(w), 1594(s), 1544(s), 1342(s), 1126(s). **EI MS**: m/z: 262 (8 %, M^+); 108 (20 %, $M^+ - {O_2S-tolyl}$).

Preparation of complexes

The complexes were obtained by following an electrochemical procedure [23, 24]. 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 (HL) or of a mixture of the ligand and the coligand [2,2'-bipyridine or 1,10phenanthroline monohydrate (L')], containing about 20 mg of tetraethylammonium perchlorate as a current carrier, was electrolysed using a platinum wire as the cathode and a cadmium 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 volts allowed sufficient current flow for smooth dissolution of the cadmium metal. The current was maintained at 10 mA during one hour. In all cases, hydrogen was evolved from the cathode. These cells can be summarised as:

 $Cd_{(+)}/CH_3CN+HL+L'/Pt_{(-)}$

After electrolysis the colourless solutions were filtered to remove any particles of metal and then left to concentrate, yielding crystalline products. The solids were washed with acetonitrile and diethyl ether and dried at room temperature.

 $[\mathit{Cd}(\mathit{Ts6mepy})_2]$. Electrochemical oxidation of a cadmium anode in a solution of the ligand N-(6-methyl-2-pyridyl)-*p*-toluenesulfon-amide, (0.19 g, 0.75 mmol) in acetonitrile (50 cm³), at 7 V and 10 mA for 2 hour caused 33.9 mg of cadmium to be dissolved, $E_f{=}$ 0.41 mol $\cdot F^{-1}$. Anal.: Calc. for $CdC_{26}H_{26}N_4O_4S_2$: C, 49.2; H, 4.1; N, 8.8; S, 10.1. Found: C, 50.2; H, 4.5; N, 9.2; S, 9.7 %.

IR (KBr, cm⁻¹): 2931 (w), 1593 (m), 1459 (s), 1322 (m), 1138 (s).

[Cd(Ts6mepy)₂bipy]. Electrolysis of a solution of the ligand (0.19 g, 0.75 mmol) and 2,2'-bipyridine (0.06 g, 0.37 mmol) in acetonitrile, (50 cm³) at 8 V and 10 mA for 2 hour dissolved 30.9 mg of cadmium, $E_f = 0.37 \text{ mol} \cdot F^{-1}$.Anal. Calc. for CdC₃₆H₃₄N₆O₄S₂: C, 54.7; H, 4.3; N, 10.6; S, 8.1.Found: C, 54.4; H, 4.3; N, 10.7; S, 7.8 %. Suitable crystals for X-ray studies were obtained by air concentration of the resulting solution.

IR (KBr, cm⁻¹): 2922 (w), 1590 (s), 1455 (s), 1321 (s), 1135 (s), 767 (m), 738 (m). ¹**H NMR** (CDCl₃, ppm): δ 9.8–6.4 (m, 22H), 2.2 (s, 6H, Me(py)), 2.1 (s, 6H, *p*-Me(Tos)). LSIMS (*m*/*z*): 790 [Cd(Ts6mepy)₂bipy]⁺; 531 [Cd(Ts6mepy)bipy]⁺; 263 (Ts6mepy)⁺.

 $[Cd(Ts6mepy)_2phen]$. A solution of the ligand (0.15 g, 0.56 mmol) and 1,10-phenantroline (0.05 g, 0.28 mmol) in acetonitrile (50 cm³) was electrolyzed at 6 V and 10 mA during 1.5 hour; 37.0 mg of

cadmium metal was dissolved from the anode, $E_f = 0.59 \text{ mol} \cdot \text{F}^{-1}$. Anal. Calc. For CdC₃₈H₃₄N₆O₄S₂ : C, 56.0; H, 4.2; N, 9.7; S, 7.8. Found: C, 55.2; H, 4.0; N, 9.9; S, 7.8 %.

IR (KBr, cm⁻¹): 2930 (w), 1590 (m), 1515 (w), 1455 (s), 1323 (m), 1138 (s), 847 (m), 727 (w). ¹H NMR (CDCl₃, ppm): δ 10.2–6.4 (m, 22H),2.2 (s, 6H, Me(py)), 2.1 (s, 6H, *p*-Me(Tos)). LSIMS (*m*/*z*): 816 [Cd(Ts6mepy)₂phen]⁺; 555 [Cd(Ts6mepy)phen]⁺.

 $[Cd(Ms6mepy)_2]$. A solution of the ligand N-(6-methyl-2-pyridyl)mesitylenesulfonamide, (0.22 g, 0.75 mmol) in acetonitrile (50 cm³) was electrolyzed at 7 V and 10 mA during 2 hour; 32.2 mg of cadmium were dissolved from the anode, $E_f = 0.38 \text{ mol} \cdot \text{F}^{-1}$. Anal. Calc. for CdC₃₀H₃₄N₄O₄S₂: C, 52.1; H, 4.9; N, 8.1; S, 9.3. Found: C, 50.5 H, 4.7 N, 7.8 S, 9.5 %. Suitable crystals for X-ray studies were obtained by air concentration of the resulting solution.

IR (KBr, cm⁻¹): 2934 (w), 1616 (m), 1458 (s), 1324 (m), 1134 (s). LSIMS (m/z): 693 [Cd(Ms6mepy)₂]⁺; 402 [Cd(Ms6 mepy)]⁺; 291 (Ms6mepy)⁺.

[*Cd*(*Ms6mepy*)₂*bipy*]. Electrolysis of a solution of the ligand (0.22 g, 0.75mmol) and 2,2'-bipyridine (0.06 g, 0.37 mmol) in acetonitrile, (50 cm³) at 13 V and 10 mA for 2 hour dissolved 33.3 mg of cadmium, $E_f = 0.39 \text{ mol}\cdot\text{F}^{-1}$. Anal. Calc. for CdC₄₀H₄₂N₆O₄S₂:C, 56.6; H, 5.0; N, 9.9; S, 7.5. Found: C, 56.5; H, 5.3; N, 9.7; S, 7.5 %.

IR (KBr, cm⁻¹): 2932 (w), 1616 (s), 1456 (m), 1323 (w), 1137 (s), 779 (m), 735 (m). ¹H NMR (CDCl₃, ppm): δ 9.6–6.4 (m, 18H), 2.32(s, 12H, *o*-Me(Tos)), 2.29(s, 6H, Me(py)), 2.22(s, 6H, *p*-Me(Tos)). LSIMS (*m*/*z*): 849 [Cd(Ms6mepy)₂bipy]⁺; 291 (Ms6mepy)⁺.

[Cd(Ms6mepy)_phen]. A solution of the ligand (0.22 g, 0.75 mmol) and 1,10-phenantroline (0.07 g, 0.37 mmol) in acetonitrile (50 cm³) was electrolyzed at 9 V and 10 mA during 2 hour; 38.3 mg of cadmium metal was dissolved from the anode, E_f = 0.46 mol·F⁻¹. Anal. Calc. for CdC₄₂H₄₂N₆O₄S₂: C, 57.8; H, 4.8; N, 9.6; S, 7.3. Found: C, 57.8; H, 5.2; N, 9.6; S, 7.3 %.

IR (KBr, cm⁻¹): 2930 (w), 1591 (m), 1516 (w), 1455 (s), 1322 (m), 1131 (s), 848 (m), 726 (w). ¹H NMR (CDCl₃, ppm): δ 9.9–6.5 (m, 18H), 2.31(s, 12H, *o*-Me(Tos)), 2.26(s, 6H, Me(py)), 2.20(s, 6H, *p*-Me(Tos)). LSIMS (*m*/*z*): 873 [Cd(Ms6mepy)₂phen]⁺; 291 [Ms6mepy]⁺.

 $[Cd(Ts3mepy)_2]$. Electrochemical oxidation of a cadmium anode in a solution of N-(3-methyl-2-pyridyl)-*p*-toluenesulfonamide, (0.15 g, 0.56 mmol) in acetonitrile (50 cm³), at 6 V and 10 mA for 2 hour, caused 35.2 mg of cadmium to be dissolved, $E_f =$ 0.42 mol· F^{-1} . During the electrolysis hydrogen was evolved at the cathode. Anal. Calc. for CdC₂₆H₂₆N₄O₄S₂: C, 49.2; H, 4.1; N, 8.8; S, 10.1. Found: C, 48.5; H, 4.2; N, 8.7; S, 9.8 %.

IR (KBr, cm⁻¹): 2921 (w), 1594(s), 1417 (m), 1312 (w), 1123 (s). ¹HNMR (CDCl₃, ppm): δ 7.8–6.5 (m, 14H), 2.4 (s, 6H, *p*-Me(Tos)), 2.1 (s, 6H, Me(py)). LSIMS (*m*/*z*): 635 [Cd(Ts3mepy)₂]⁺; 263 (Ts3mepy)⁺.

[*Cd*(*Ts3mepy*)₂*bipy*]. Electrolysis of a solution of the ligand (0.19 g, 0.75 mmol) and 2,2'-bipyridine (0.06 g, 0.37 mmol) in acetonitrile, (50 cm³) at 8 V and 10 mA for 2 hour dissolved 44.6 mg of cadmium, $E_f = 0.53 \text{ mol}\cdot\text{F}^{-1}$. Anal. Calc. for CdC₃₆H₃₄N₆O₄S₂: C, 54.7; H, 4.3; N, 10.6; S, 8.1.Found: C, 54.2; H, 4.5; N, 10.5; S, 8.0 %. Suitable crystals for X-ray studies were obtained by air concentration of the acetonitrile solution.

IR (KBr, cm⁻¹): 2916 (w), 1597 (s), 1414 (s), 1326 (m), 1114 (m), 769 (m), 738(m). ¹H NMR (CDCl₃, ppm): $\delta 8.8-6.7$ (m, 22H), 2.3 (s, 6H, *p*-Me(Tos)), 2.0 (s, 6H, Me(py)). LSIMS (*m*/*z*): 790 [Cd(Ts3mepy)₂bipy]⁺; 531 [Cd(Ts3mepy)bipy]⁺; 263 (Ts3mepy)⁺.

 $[Cd(Ts3mepy)_2phen]$. A similar experiment to that described above (10 V, 10 mA, 1.5 h.) with the same sulfonamine ligand (0.15 g, 0.56 mmol) and 1,10-phenantroline (0.05 g, 0.28 mmol) in

acetonitrile (50 cm³) led to the dissolution of 32.2 mg of cadmium, $E_f = 0.51 \text{ mol} \cdot \text{F}^{-1}$. Anal. Calc. for CdC₃₈H₃₄N₆O₄S₂: C, 56.0; H, 4.2; N, 9.7; S, 7.8. Found: C, 55.8; H, 4.9; N, 10.3; S, 7.3 %.

IR (KBr, cm⁻¹): 2922 (w), 1594 (s), 1519 (m), 1399 (m), 1324 (m), 1117 (m),843 (s), 727 (w). LSIMS (m/z): 816 [Cd(Ts3mepy)₂ phen]⁺; 555 [Cd(Ts3mepy) phen]⁺; 263 (Ts3mepy)⁺.

 $[Cd(Ms3mepy)_2]$. A solution of the ligand N-(6-methyl-2-pyridyl)mesitylenesulfonamide, (0.14 g, 0.50 mmol) in acetonitrile (50 cm³) was electrolyzed at 7 V and 10 mA during 1.5 hour; 34.5 mg of cadmium were dissolved from the anode, $E_{\rm f}=0.55~{\rm mol}\cdot F^{-1}$. Anal. Calc. for $CdC_{30}H_{34}N_4O_4S_2$: C, 52.1; H, 4.9; N, 8.1; S, 9.3. Found: C, 49.2 H, 4.7 N, 7.6 S, 9.4 %.

IR (KBr, cm⁻¹): 2932 (w), 1602 (m), 1452 (m), 1320 (m), 1123 (m).

[Cd(M3mepy)₂bipy]. Electrolysis of a solution of the ligand (0.16 g, 0.57 mmol) and 2,2'-bipyridine (0.04 g, 0.29 mmol) in acetonitrile, (50 cm³) at 5 V and 10 mA for 1.5 hour dissolved 31.2 mg of cadmium, $E_f = 0.50 \text{ mol}\cdot\text{F}^{-1}$. Anal. Calc. for CdC₄₀H₄₂N₆O₄S₂:C, 56.6; H, 5.0; N, 9.9; S, 7.5. Found: C, 56.6; H, 4.9; N, 10.0; S, 7.1 %. Suitable crystals for X-ray studies were obtained by air concentration of the resulting solution.

IR (KBr, cm⁻¹): 2931 (w), 1597 (s), 1440 (s), 1315 (m), 1119 (m), 767 (m), 738 (m). ¹**H NMR** (CDCl₃, ppm): δ 8.7–6.5 (m, 18H), 2.7(s, 12H, *o*-Me(Tos)), 2.3(s, 6H, *p*-Me(Tos)), 2.1(s, 6H, Me(py)).

[Cd(Ms3mepy)_phen]. A solution of the ligand (0.16 g, 0.57 mmol) and 1,10-phenantroline (0.05 g, 0.29 mmol) in acetonitrile (50 cm³) was electrolyzed at 5 V and 10 mA during 2 hour; 41.8 mg of cadmium metal was dissolved from the anode, E_f = 0.50 mol·F⁻¹. Anal. Calc. for CdC₄₂H₄₂N₆O₄S₂: C, 57.8; H, 4.8; N, 9.6; S, 7.3. Found: C, 58.1; H, 4.8; N, 9.7; S, 7.2 %.

IR (KBr, cm⁻¹): 2934 (w), 1594 (m), 1518 (w), 1416 (s), 1320 (m), 1118 (m), 843 (m), 728 (m). ¹H NMR (CDCl₃, ppm): δ 9.3–6.6 (m, 18H), 2.4(s, 12H, *o*-Me(Tos)), 2.2(s, 6H, *p*-Me(Tos)), 1.8(s, 6H, Me(py)). LSIMS (*m*/*z*): 873 [Cd(Ms3mepy)₂phen]⁺; 581 [Cd(Ms3mepy)phen]⁺; 291 [Ms3mepy]⁺.

Physical measurements

The C, N, H and S contents of the compounds were determined on a Carlo-Erba EA 1108 microanalyser. IR spectra were recorded as KBr mulls on a Bruker Vector-22 spectrophotometer. The ¹H NMR spectra of the compounds were recorded on a Bruker ARX-400 MHz spectrometer using CDCl₃ as solvent. EI (70 eV, 250 °C) and LSI mass spectra were recorded on a Micromass VG Autospec M instrument.

Crystal structure determination

The data collections were taken on a SIEMENS Smart CCD areadetector diffractometer with graphite-monochromated Mo-K_{α} radiation. Absorption corrections were carried out using SADABS [25]. All the structures were solved by direct methods and refined by full-matrix least-squares based on F² [26]. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the case of HMs6mepy, hydrogen atoms were located on a difference electron density map and refined with isotropic displacement parameters – except those of the methyl groups, which were included in idealised positions and refined with isotropic displacement parameters. For all the complexes, hydrogen atoms were also included in idealised positions and refined with isotropic displacement parameters – except those in the coordinated water molecule of [Cd(Ts6mepy)₂(H₂O)₂]H₂O, 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 [27].

Supplementary material

The atomic positions, full list of bond lengths and angles and other crystallographic data are available on request from J.C. Crystallographic data have been deposited with the CCDC, (12 Union Road, Cambridge CB2 1EZ, UK) and are available on request quoting the deposition numbers 192777 and 187517 to 187520.

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