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Synthesis of cobalt(II), nickel(II) and copper(II) complexes with 2-(2hydroxyphenyliminomethyl)-1-(4-methyl-phenylsulfonamido)benzene and crystal structures of {bis(methanol)[2-(2'-*N*tosylaminophenyl)iminomethyl]phenolato}nickel(II) and {bis(2,2'bipyridine)[2-(2'-*N*-tosylaminophenyl)iminomethyl]phenolato}copper(II)

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Abstract

Electrochemical oxidation of metal anodes (cobalt, copper and nickel) in acetonitrile solutions of 2-(2-hydroxyphenyliminomethyl)-1-(4-methyl-phenylsulfonamido)benzene (H₂L) gave [CoL], [CuL] and [NiL] complexes. When 1,10-phenanthroline (phen) or 2,2'bipyridine (bipy) was added to the electrolytic cell, the mixed complexes [MLL'] (M=Co, Cu, L'=bipy or M=Ni, L'=phen) were obtained. A binuclear compound of composition $[Ni_2L_2(MeOH)_4]$ (1) was synthesized by reaction of the ligand H₂L and nickel(II) acetate in methanol. X-ray structure determination showed the compound to be binuclear, with each nickel atom coordinated to two nitrogen and two bridging phenol oxygen atoms of two dianionic ligands and two methanol molecules, in an octahedral environment. The crystal structure of [CuLbipy] (2) was determined by X-ray diffraction; with the copper atom in a distorted bipyramidal environment defined by the two bipyridine nitrogen atoms and by the phenolic oxygen and the nitrogen atoms of the dianionic ligand. The electronic and vibrational spectral data of the complexes are discussed and related to the structure. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Most ligands of type I [1,2] are binuclear compounds of types II [3–6] and III [7–10] with bridging phenolato oxygen groups, although there many examples of mononuclear structures such as IV [10–19]. In the case of vanadium, a compound formed by two monomer fragments bridged by an oxo group, V, has been described [20].

Until recently, most of the tridentate dianionic ligands were salyciliden-2-aminophenol derivatives, I (X=Y=O) [1,7,10,11,21–24]. In the last few years, some studies on these types of ligands with X=O, but Y=S or Se have been carried out [12,17,25–28]. However, as far as we know, coordination compounds of 2-(2-hydroxy-

phenyliminomethyl)-1-(4-methyl-phenylsulfonamido)benzene (X=O, Y=NTs), H_2L were hitherto unknown.

In this paper, the synthesis of cobalt(II), nickel(II) and copper(II) complexes of H_2L and the crystal structures of $[Ni_2L_2(MeOH)_4]$ and [CuL(bipy)] are described.

2. Experimental

All solvents and 2-hydroxyaniline were commercial products used without further purification.

2-(2-Hydroxyphenyliminomethyl)-1-(4-methyl-phenylsulfonamido)benzene (H₂L) was prepared by refluxing 2formyl-1-(4-methylphenylsulfonamido)benzene [29] (2.75 g, 10 mmol) and 2-hydroxyaniline (1.09 g, 10 mmol) in benzene (20 cm³) as solvent until the theoretical amount of water was collected in a Dean-Stark trap. The resulting

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solution was concentrated in a rotary evaporator to a final volume of 5 cm³ and the solid was precipitated by the addition of 10 cm³ of methanol. Recrystallization from hot methanol yielded yellow crystals (2.75 g; yield, 75%). Anal. Found: C, 65.6; H, 5.0; N, 7.9; S, 8.9. Calc. for $C_{20}H_{18}N_2O_3S$: C, 65.6; H, 5.0; N, 7.6; S, 8.8%. IR, ν (NH) 3400, ν (OH) 3100–2800, ν (C=N) 1610, $\nu_{as}(SO_2)$ 1322 and $\nu_s(SO_2)$ 1140 cm⁻¹.

2.1. Preparation of complexes

The complexes were obtained following an electrochemical procedure [30]. An acetonitrile solution of the ligand containing about 15 mg of tetramethylammonium perchlorate as a current carrier was electrolyzed using a platinum wire as the cathode and a metal plate as the sacrificial anode. The cell can be summarized as $Pt(-)/MeCN+H_2L/M(+)$; M=Co, Cu, Ni.

2.2. Cobalt(II) complex

2.2.1. [CoL].CH₃CN

The electrochemical oxidation of cobalt in a solution of H_2L (0.136 g, 0.371 mmol) in CH_3CN (50 M) containing 20 mg of tetramethylammonium perchlorate for 2 h at 10 V and 10 mA resulted in the loss of 22.8 mg of cobalt from the anode (E_f =0.52). Hydrogen was evolved at the cathode during the electrolysis. The room temperature concentration of the reaction mixture produced a microcrystalline dark brown precipitate, which was collected by filtration and identified as [CoL].CH₃CN. Anal.: calculated for [CoC₂₂H₁₉N₃SO₃]: C, 56.90, N, 9.05, H, 4.12%. Found: C, 56.93, N, 9.06, H, 4.19%. IR, ν (C=N) 2190, ν (C=N) 1600, ν_{as} (SO₂) 1290 and ν_s (SO₂) 1160 cm⁻¹.

2.3. Nickel(II) complexes

2.3.1. [NiL]

A brown powder was isolated from the solution resulting from the electrolysis (20 V, 10 mA, 2 h) of a solution of H₂L (0.136 g; 0.371 mmol) in 50 cm³ of CH₃CN using a nickel anode. Under these conditions, 21 mg of nickel were dissolved (E_f =0.48). The precipitate was collected, washed with acetonitrile and diethyl ether, dried in vacuo and identified as [NiL]. Anal.: calculated for [NiC₂₀H₁₆N₂SO₃]: C, 56.76, N, 6.62, H, 3.78%. Found: C, 56.27, N, 6.55, H, 3.18%. IR, ν (C=N) 1590, ν_{as} (SO₂) 1280 and ν_s (SO₂) 1155 cm⁻¹.

2.3.2. $[Ni_2L_2(MeOH)_4]$

This compound was alternatively obtained by the slow addition of 2-(2-hydroxyphenyliminomethyl)-1-(4-methyl-phenylsulfonamido)benzene (0.36 g, 1 mmol) in methanol (15 cm³) to a solution of nickel acetate (0.248 g, 1 mmol) in the same solvent (10 cm³). After refluxing for 1 h, the brown crystalline precipitate was filtered and washed with

methanol. The solid was recrystallized in the same solvent and brown crystals, suitable for X-ray studies, were obtained and characterized as $C_{44}H_{48}N_4O_{10}S_2Ni_2$. Anal. calculated: C, 54.8; H, 5.0; N, 5.8; S, 6.7. Found: C, 55.1; H, 5.0; N, 5.6; S, 6.8%. IR, ν (C=N) 1593, ν_{as} (SO₂) 1286 and ν_s (SO₂) 1173 cm⁻¹.

2.3.3. [NiLphen]

The electrolysis of a solution containing 0.136 g (0.371 mmol) of H₂L and 0.073 g (0.371 mmol) of 1,10-phenanthroline in 50 cm³ of CH₃CN for 2 h and using a current of 16 V, 10 mA dissolved 22.1 mg of nickel metal (E_f =0.50). The product of the reaction was a brown precipitate, which was isolated following the same procedure as described above. Anal: calculated for [NiLphen], [C₃₂H₂₄NiN₄SO₃]: C, 63.67, N, 9.28, H, 3.97%. Found: C, 63.30, N, 9.48, H, 3.78%. IR, ν (C=N) 1590, ν_{as} (SO₂) 1280 and ν_s (SO₂) 1155 cm⁻¹.

2.4. Copper(II) complexes

2.4.1. [CuL]

Electrolysis of a solution of H₂L (0.136 g, 0.371 mmol) and tetramethylammonium perchlorate (20 mg) in CH₃CN (50 cc) for 2 h at 6 V and 10 mA using a copper anode led to the dissolution of 46.2 mg of copper (E_f =0.97). Brown crystals of [CuL] were isolated from the resulting solution. Anal.: calculated for [C₂₀H₁₆CuN₂SO₃]: C, 56.13, N, 6.53, H, 3.78%. Found: C, 55.70, N, 6.54, H, 3.74%. IR, ν (C=N) 1590, ν_{as} (SO₂) 1285 and ν_s (SO₂) 1170 cm⁻¹.

2.4.2. [CuLbipy]

The electrolysis of an acetonitrile solution containing H_2L (0.136 g, 0.371 mmol) and 2,2'-bipyridine (0.058 g, 0.371 mmol), using a current of 11 V and 10 mA over 2 h, resulted in the loss of 44.9 mg of copper (E_f =0.94). Brown crystals of [CuLbipy] that were suitable for X-ray studies were isolated from the reaction solution. Anal.: calculated for [C₃₀H₂₄CuN₄SO₃]: C, 61.65, N, 9.59, H, 4.11%. Found: C, 61.94, N, 9.72, H, 4.01%. IR, ν (C=N) 1600, ν_{as} (SO₂) 1285 and ν_{s} (SO₂) 1160 cm⁻¹.

2.5. Physical measurements

Microanalyses were performed using a Carlo-Erba EA1108 microanalyser. IR spectra were recorded in KBr disks on a Perkin-Elmer 180 spectrophotometer.

The magnetic susceptibility for $[Ni_2L_2(MeOH)_4]$ was measured by the Faraday method in the temperature range 78–300 K (Table 1), using Hg[Co(CNS)_4] as the calibrant.

The exchange parameter, J, was deduced from a leastsquares fitting procedure by minimizing the deviation from the experimental values of the calculated theoretical magnetic susceptibilities using the equation.

Table 1 Magnetic data for $[Ni_2L_2(MeOH)_4]^a$

T (K)	$\chi_{\rm M}$ ^b exp.	$\mu_{\rm eff}$ ^c (exp.) B.M.	$\chi_{\rm M}$ ^b calc.	$\mu_{\rm eff}$ (calc.) B.M.
290	7311	2.91	7156	2.88
269	7820	2.90	7680	2.88
251	8235	2.88	8196	2.87
233	8710	2.85	8789	2.86
216	9540	2.87	9437	2.86
199	10 251	2.86	10 191	2.85
185	11 081	2.86	10 910	2.84
170	11 555	2.80	11 806	2.83
159	12 385	2.81	12 565	2.83
150	12 741	2.77	13 264	2.82
132	14 638	2.78	14 927	2.81
98	19 210	2.74	19 583	2.77
89	21 571	2.77	21 348	2.76
83	23 010	2.76	22 713	2.75

^a $J = -4 \text{ cm}^{-1}$; g = 2.03; estimated error r = 1.83%.

^b $\chi_{\rm M}$, molar magnetic susceptibility.

^c $\mu_{\rm eff}$, per one nickel (II) atom in a binuclear molecule.

$$\chi_{\rm M} = \frac{3g^2}{4T} \frac{{\rm e}^{-4J/KT} + 5}{{\rm e}^{-6J/KT} + 3{\rm e}^{-4J/KT} + 5}$$

where g, T and K have their usual meanings.

2.6. X-ray data collection and processing

The crystal data and a summary of the data collection and structure refinement for these compounds are given in Table 2. Crystals of complexes $[NiL(MeOH)_4]$ (1) and [CuLbipy] (2) were mounted on glass fibres and data were

Table 2

Summary of crystal data for $[\rm Ni_2L_2(MeOH)_4]$ (1) and [CuLbipy] (2)

	[Ni ₂ L ₂ (MeOH) ₄]	[CuLbipy]
Empirical formula	$C_{44}H_{48}N_4O_{10}S_2Ni_2$	C ₃₀ H ₂₄ CuN ₄ O ₃ S
Formula weight	974.5	584.13
Size	$0.1 \times 0.08 \times 0.05$	$0.75 \times 0.60 \times 0.20$
Crystal system	Triclinic	Monoclinic
Space group	P−1 (#2)	P2(1)/c
Unit cell dimensions,		
<i>a</i> , Å	10.271(2)	17.2716(9)
<i>b</i> , Å	10.523(2)	8.6945(4)
<i>c</i> , Å	11.460(2)	17.9165(9)
<i>α</i> , °	113.59(3)	90
<i>β</i> , °	105.21(3)	92.7220(10)
γ, °	91.03(3)	90
Volume, Å ³	1084.7(4)	2687.4(2)
Ζ	1	4
$d_{\rm calc}, {\rm g \ cm}^{-3}$	1.492	1.444
λ , Å (MoK α radiation)	0.71073	0.71073
μ (MoK α), mm ⁻¹	1.027	0.930
Т, К	293(2)	298(2)
no. of reflns collected	1523	23 409
no. of indept. reflns.	1400	9901
F(000)	508	1204
R^{a}	0.070	0.0591
<i>R</i> w ^b	0.1447	0.1131

 ${}^{a}R = \Sigma(|Fo| - |Fc|)/\Sigma|Fo|$. ${}^{b}R_{w} = [(\Sigma w(|Fo| - |Fc|)^{2}/\Sigma w|Fo|^{2}]^{1/2}$.

recorded on a Syntex P2₁ automatic diffractometer for (1) and on a Siemens CCD Smart system for (2), with graphite monocromated MoK α radiation (λ =0.71073 Å) at 298 and 293 K using the $\omega/2\theta$ scan technique, $2\theta_{max} = 56^{\circ}$ for (1) and 66.3 for (2). 1523 reflections were collected, of which, 1367 with $I > 2\sigma I$ were used for calculations for (1) and 23 409, of which, 9901 with $I > 2\sigma I$ for (2).

The structure of (1) was solved by the heavy-atom method and that of (2) by the direct method. In both compounds, non-hydrogen atoms and hydrogen atoms, except for those from CH₃ groups, were located from Fourier difference synthesis. The structures were refined using a full-matrix least-squares technique, isotropically for the hydrogen atoms and anisotropically for all remaining non-hydrogen atoms. All calculation were performed using SHELXS-93 [31] for (1) and SHELXS-97 [32] for (2). Interatomic bond distances and angles are given in Tables 3 and 4, respectively. Atom positions, bond lengths and bond angles, and other crystallographic data, have been deposited as Supplementary Publication No. CSD 59422 for (1) and 408953 for (2): copies can be obtained through Fachinformationszentrum Karlsruhe, 76344, Energie Physik Mathematik, D-7514 Eggenstein-Leopolshafen.

3. Results and discussion

The electrochemical oxidation of cobalt, copper and nickel in the presence of the Schiff base H_2L led to complexes of general formulae [ML], where L stands for the dianionic form of the Schiff base.

For cobalt and nickel, the electrochemical efficiency, $E_{\rm f}$, defined as moles of metal dissolved per Faraday of charge, was close to 0.5 mol F⁻¹, in accordance with the following process:

Table 3										
Selected	bond	distances	(Å)	and	angles	(°)	for	[Ni ₂ L ₂ (MeOH)₄]

Ni–N(1)	2.002(12)	Ni–N(2)	2.093(13)
Ni–O(3)	2.051(11)	Ni-O(3')	2.063(10)
Ni–O(4)	2.111(14)	Ni–O(5)	2.191(13)
S-N(2)	1.602(14)	S-O(1)	1.419(12)
S-O(2)	1.460(12)	S-C(14)	1.77(2)
N(1)-C(6)	1.41(2)	N(1)-C(7)	1.30(2)
N(2)-C(13)	1.41(2)	O(3)–C(1)	1.33(2)
O(4)–C(21)	1.43(2)	O(5)-C(22)	1.40(2)
C(1)–C(2)	1.37(2)	C(1)–C(6)	1.42(2)
C(2)–C(3)	1.37(2)	C(3)–C(4)	1.38(2)
C(4)–C(5)	1.36(2)	C(5)-C(6)	1.40(2)
C(7)–C(8)	1.46(2)	C(17)-C(20)	1.51(2)
N(1)-Ni-N(2)	87.3(4)	N(1)-Ni-O(3)	79.7(4)
N(1)-Ni-O(3')	159.0(4)	N(1)-Ni-O(4)	94.6(5)
N(1)-Ni-O(5)	94.8(5)	N(2)-Ni-O(3)	166.9(4)
N(2)-Ni-O(3')	113.6(4)	N(2)-Ni-O(4)	94.2(6)
N(2)-Ni-O(5)	92.3(5)	O(3)-Ni-O(3')	79.4(5)
O(3)-Ni-O(4)	86.8(5)	O(3)-Ni-O(5)	89.0(4)
O(3')-Ni-O(4)	86.7(4)	O(3')–Ni–O(5)	82.4(4)
O(4)-Ni-O(5)	168.8(4)	N(2)-S-O(1)	115.3(8)
N(2)-S-O(2)	106.3(7)	N(2)-S-C(14)	105.2(6)
O(1)-S-O(2)	113.9(7)	O(1)-S-C(14)	107.6(7)
O(2)-S-C(14)	107.9(8)	Ni-N(1)-C(6)	113.5(8)
Ni-N(1)-C(7)	125.9(11)	Ni-N(2)-C(13)	117.4(9)
S-N(2)-C(13)	118.5(10)	Ni-O(3)-Ni'	100.6(4)
Ni-O(3)-C(1)	112.7(9)	Ni-O(4)-C(21)	124.1(11)
Ni-O(5)-C(22)	121.4(11)	N(1)-C(6)-C(1)	113.1(13)
N(1)-C(7)-C(8)	125.1(14)	C(7)-C(8)-C(13)	125(2)
N(2)-C(13)-C(8)	120(2)		

Cathode:
$$H_2L + 2e^- \rightarrow L^{2-} + H_2$$

Anode: $L^{2-} + M \rightarrow [ML] + 2e^-$
or $L^{2-} + Ni + phen \rightarrow [NiLphen] + 2e^-$

In the case of copper, $E_{\rm f}$ was close to 1 mol F⁻¹, indicating that the formation of copper (I) at the anode is followed by oxidation to copper (II) in solution. This behaviour has already been observed in other copper systems in which low-oxidation-state species are the initial electrochemical products. This fact suggests that a possible mechanism could be:

Cathode:
$$H_2L + e^- \rightarrow HL^- + \frac{1}{2}H_2$$

Anode: $Cu \rightarrow Cu^+ + e^-$
 $Cu^+ + HL^- \rightarrow [CuL] + \frac{1}{2}H_2$
or $HL^- + Cu^+ + bipy \rightarrow [CuLbipy] + \frac{1}{2}H_2$

3.1. Structure of $[Ni_2L_2(MeOH)_4]$

The analytical data of the compound obtained by reaction of nickel acetate and 2-(2-hydroxyphenyliminomethyl)-1-(4-methyl-phenylsulfonamido) benzene, H₂L, in methanol are compatible with a NiL· 2MeOH formulation. An X-ray diffraction study of this compound showed that it consists of discrete neutral dinuclear centrosymmetric $[Ni_2L_2(MeOH)_4]$ units (Fig. 1) with a 3.165 (1) Å intermetallic Ni ... Ni distance. Each nickel atom is coordinated to two nitrogen and two oxygen atoms from the ligands and two oxygen atoms from two methanol molecules. Both nickel atoms are bridged by two phenol oxygen atoms. The donor atoms [N(1), N(2), O(3)]of one tridentate ligand and the oxygen bridge atom of the other ligand (O(3)') are coplanar and occupy the equatorial positions of a tetragonally distorted pseudo-octahedral nickel(II) centre, with two methanol ligands at the axial sites. The deviation from perfect geometry around the nickel atom is illustrated by the values of the angles defined by the nickel atom and two equatorial cis donor atoms, which are very different from the expected value of 90° [N(1)-Ni-O(3)=79.7(4)°]. On the other hand, the NiN(1)O(3), O(3)C(1)C(16)N(1) fragments and the phenyl ring C(1)-C(6) form dihedral angles with $[Ni_2O(3)]_2$ of 2, 11 and 19°, respectively. In the same way, the six-membered chelate ring NiN(1)C(7)C(8)C(13)N(2)and the phenyl ring C(8)-C(13) are not coplanar with the plane NiO(3)NiO(3)'. In addition, the dihedral angles between the N(1)NiN(2) fragment and the C(8)–C(13) phenyl ring with the NiO(3)NiO(3)' plane are 2 and 4° , respectively. The dihedral angle between the phenyl ring C(14)-C(19) and the central square $Ni_2(O(3))_2$ is 54°.

The Ni–N_{imine} distance of 2.002(12) Å is slightly shorter than those found in other hexacoordinate salicylidenealdiminate nickel(II) complexes [2.050(6)-

Table 4 Selected bond lengths (Å) and angles (°) for [CuLbipy]

Cu(1)–O(1)	1.9403(17)	Cu(1)–N(1)	1.9737(17)
Cu(1) - N(2)	2.003(2)	Cu(1) - N(4)	2.0037(18)
Cu(1)–N(3)	2.354(2)	S(1)–O(3)	1.4448(18)
S(1)-O(2)	1.4482(18)	S(1) - N(2)	1.5950(18)
S(1)-C(14)	1.774(2)	N(1)-C(7)	1.281(3)
N(1)-C(6)	1.415(3)	N(2)-C(13)	1.407(3)
N(3)-C(21)	1.340(4)	N(3)-C(25)	1.343(3)
N(4)-C(30)	1.330(3)	N(4)-C(26)	1.347(3)
O(1)–C(1)	1.314(3)	C(1) - C(2)	1.403(3)
C(1)-C(6)	1.420(3)	C(2) - C(3)	1.386(4)
C(3)–C(4)	1.392(4)	C(4) - C(5)	1.387(3)
C(5)-C(6)	1.391(3)	C(7)–C(8)	1.451(3)
C(8)–C(9)	1.401(3)	C(8)–C(13)	1.428(3)
C(9)-C(10)	1.381(4)	C(10)-C(11)	1.379(4)
C(11)-C(12)	1.383(4)	C(12)-C(13)	1.393(3)
C(14)-C(15)	1.378(4)	C(14)–C(19)	1.385(4)
C(15)-C(16)	1.387(4)	C(16)-C(17)	1.379(5)
C(17)-C(18)	1.373(5)	C(17)-C(20)	1.509(5)
C(18)-C(19)	1.381(5)	C(21)-C(22)	1.390(5)
C(22)-C(23)	1.368(6)	C(23)-C(24)	1.369(6)
C(24)-C(25)	1.395(4)	C(25)-C(26)	1.475(4)
C(26)-C(27)	1.396(4)	C(27)-C(28)	1.373(5)
C(28)-C(29)	1.362(5)	C(29)-C(30)	1.383(3)
O(1)-Cu(1)-N(1)	84.24(7)	O(1)-Cu(1)-N(2)	154.69(9)
N(1)-Cu(1)-N(2)	86.30(7)	O(1)-Cu(1)-N(4)	92.00(7)
N(1)-Cu(1)-N(4)	173.92(8)	N(2)-Cu(1)-N(4)	99.04(8)
O(1)-Cu(1)-N(3)	114.61(8)	N(1)-Cu(1)-N(3)	101.63(8)
N(2)-Cu(1)-N(3)	90.27(8)	N(4)-Cu(1)-N(3)	75.57(8)
O(3)-S(1)-O(2)	115.88(12)	O(3)-S(1)-N(2)	106.12(11)
O(2)-S(1)-N(2)	114.53(11)	O(3)-S(1)-C(14)	107.67(11)
O(2)-S(1)-C(14)	106.69(11)	N(2)-S(1)-C(14)	105.28(10)
C(7)-N(1)-C(6)	124.37(18)	C(7)-N(1)-Cu(1)	123.89(15)
C(6)-N(1)-Cu(1)	110.88(13)	C(13)-N(2)-S(1)	120.66(16)
C(13)–N(2)–Cu(1)	117.27(14)	S(1)-N(2)-Cu(1)	120.38(11)
C(21)-N(3)-C(25)	117.5(3)	C(21)-N(3)-Cu(1)	130.7(2)
C(25)-N(3)-Cu(1)	107.59(16)	C(30)-N(4)-C(26)	119.0(2)
C(30)-N(4)-Cu(1)	121.22(17)	C(26)-N(4)-Cu(1)	119.76(16)
C(1) - O(1) - Cu(1)	112.01(14)	O(1)-C(1)-C(2)	122.5(2)
O(1)-C(1)-C(6)	119.95(19)		

2.066(3) Å] [33,34]. The Ni–N_{amide} bond distance of 2.093(13) Å is longer than the Ni–N_{imine} one and, as expected, significantly longer than those found in tetrahedral nickel amide complexes [1.916(3) [35], 1.839(6) Å [16]]. This is a reflection of the lower coordination number in these latter compounds. The Ni–O_{phenol} bond distances of 2.051(11) and 2.063(10) Å are longer than observed in mononuclear hexacoordinate salicylidenealdiminate nickel complexes [2.005(4), 2.032(3) Å] [33,34,36], whereas the other two Ni–O bonds between the metal atom and the methanol oxygen atom are considerably longer, being 2.118(14) and 2.191(13) Å. The C(7)–N(1) distance [1.30(2) Å] is as expected for azomethine C=N bonds [37]. C(1)–O(3) [1.33(2) Å] is shorter than a C–O single bond, but longer than a C=O double bond [38].

3.2. Structure of [CuLbipy]

Fig. 2 shows the molecular structure of [CuLbipy] and the atom numbering system used. Selected bond distances and angles are listed in Table 4.

The compound consists of discrete molecules with a pentacoordinated copper atom. The geometrical parameter, τ , [$\tau = (\beta - \alpha)/60$], where α and β are O(1)–Cu–N(3) and N(1)–Cu–N(4) bond angles, respectively [39], has a value of 0.9885. This suggests that the complex has a geometry closer to that of a trigonal bipyramide (τ =1) than of a square–pyramide (τ =0). The environment around the copper metal is formed by one of the bipyridine nitrogen atoms, the phenolate oxygen atom and the amide deprotonated nitrogen of the 4-toluenesulfonamide group atom, occupying the equatorial sites, and the azomethine nitrogen atom and the other bipyridine nitrogen atoms in the axial sites. The copper atom and the equatorial donor



Fig. 1. Crystal structure of {bis(methanol)[2-(2'-N-tosylaminophenyl)iminomethyl] phenolato}nickel(II).



Fig. 2. Crystal structure of {bis(2,2'-bipyridine)[2-(2'-*N*-tosylaminophenyl)iminomethyl] phenolato}copper(II).

atoms are coplanar within the limits of experimental accuracy. Distortion was observed in the equatorial plane (Table 4), with the angles O(1)-Cu-N(3), 114.61(8)°, N(3)-Cu-N(2), 90.27(8)°, and O(1)-Cu-N(2), 154.69(9)°, and along the axial direction of the trigonal bipyramide, with a N(1)-Cu-N(4) angle of 173.92(8)°.

The Cu–O bond length, 1.940(18) Å, is similar to the values observed for other five-coordinated copper complexes with Schiff-bases as ligands [14,40]. The Cu–N_{imine} bond length [1.973(17) Å] is shorter than those found in other five-coordinated copper compounds, for example, in bis(dimethylaminosalicyaldiminato)copper(II), with a mean value of 1.946 Å [40]. The Cu–N_{bipy} bond distances are different, with the axial bond, 2.0037(18)Å, being shorter than the equatorial one, 2.354(2) Å. The shorter Cu–N_{bipy} bond length is similar to the bond distances found in other five-coordinated copper(II) complexes with 2,2'-bipyridine; (2.002(4) Å in di- μ -hydroxo-bis[(2,2'-bipyridine)(trifluoromethanesulfonato-O)-copper(II)] [41].

3.3. Magnetic studies

The study of the magnetic properties of $[Ni_2L_2(MeOH)_4]$ shows that the effective magnetic moment [per nickel (II) atom] decreases with temperature down to a value that is less than the 'spin-only' value, 2.83 B.M., Table 1. This behaviour can be attributed to weak antiferromagnetic exchange interaction between two paramagnetic nickel atoms. The value of the exchange parameter J is -4 cm⁻¹. In spite of the fact that the NiO(3)NiO(3)' fragment is nearly planar, implying the overlap of equatorial plane magnetic orbitals and correspondingly strong antiferromagnetism, the relatively small J value should not be considered as anomalous. It is well known that the majority of high spin nickel (II) complexes

possessing the exchange fragment mentioned above [42–46] reveal weak exchange coupling in contrast with copper (II) complexes [46].

3.4. Spectroscopic studies

The IR data are consistent with the chelating behaviour of the ligand. The bands attributable to ν (NH) and ν (OH) are absent in the complexes, confirming the loss of the phenolic and amide group hydrogen atoms during the electrolysis. The ν (C=N) shifts to lower frequency in going from the free ligand, 1609 cm⁻¹, to the complexes, 1590–1600 cm⁻¹. These observations suggest that the Schiff base coordinates the metallic atoms in the dianionic form through the phenolate oxygen atom, and the amide and azomethine nitrogen atoms. This conclusion is confirmed by the X-ray structures of [Ni₂L₂(MeOH)₄] and [CuLbipy]. In the IR spectra of the mixed compounds, additional bands due to coordinated bipyridine and phenanthroline ligands are observed (720 and 750 cm⁻¹, and 725, 845 and 1510 cm⁻¹, respectively) [47,48].

The diffuse reflectance spectrum of the [CuL] compound shows a band at a ca. 15 000 cm⁻¹, in agreement with those reported for square–planar copper(II) complexes. A square–planar dimeric structure is therefore tentatively assigned to the copper(II) complexes.

The diffuse reflectance spectra of nickel(II) complexes exhibit two d–d bands that are well within the range for six-coordinate octahedral complexes of nickel(II) (ca. 9100–8900 and 17 500–16 100 cm⁻¹), which can be assigned to the ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ transitions respectively [49]. This octahedral environment has been found in the X-ray structure determination of [Ni₂L₂(MeOH)₄]. Consequently, a six-coordinate polymeric structure is therefore tentatively assigned to the [NiL] complex.

The cobalt complex spectrum shows three bands at 7500, 11 900 and 18 200 cm⁻¹, assigned to ${}^{4}T_{2g} \rightarrow {}^{4}T_{1g}$ (ν_{3}), ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ (ν_{2}) and ${}^{4}T_{1g}(P) \rightarrow {}^{4}T_{1g}(F)$ (ν_{3}) transitions in a distorted octahedral field, respectively [48]. Therefore, a six-coordinated polymeric structure is tentatively assigned to the cobalt(II) complex.

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