

Electrochemical synthesis of metal (II) complexes of Schiff base 2-tosylamino (2'-pyridyl)aniline: the crystal structure of bis-[2-tosylamino(2'-pyridyl)anilinato]cobalt(II)

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Abstract—Complexes of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) with the anion of the Schiff base 2-tosylamino(2'-pyridyl)aniline (HL) have been prepared by using an electrochemical procedure. These compounds were characterized by elemental analysis, IR, UV and NMR spectroscopy, and in the case of $[CoL_2]$ by X-ray diffraction methods. In this compound the cobalt(II) atom is in a distorted tetrahedral environment, each Schiff base anion acting as a bidentate ligand with the pyridine nitrogen atom uncoordinated. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: electrochemical synthesis; 2-tosylamino(2'-pyridyl)aniline; Schiff base complexes; crystal structure.

INTRODUCTION

This work continues studies of neutral complexes [1-11] of Schiff bases such as I and II where X = O, S, Se and Het = an heterocyclic ring. In these compounds, the pyridine nitrogen atom is un-coordinated although for the complexes of cobalt(II) [10] with ligand II (where X = S and Het = thiophene) and zinc(II) [11] with ligand I (where X = O) X-ray studies show a weak intramolecular secondary bond between the metallic atom and the N_{pyridine} atoms.

We have now synthesized by an electrochemical procedure Co, Ni, Cu, Zn and Cd complexes containing the ligand L, derived from I with X = NHTs. The crystal structure of bis-[2-tosylamino(2'-pyr-idyl)anilinato]cobalt(II) is also reported.

EXPERIMENTAL

Materials

The metals (Ega Chemie) were used in the form of ca 2×2 cm plates. All solvents, 2-aminopyridine and other reagents except 2-tosylaminobenzaldehyde are commercially available and were used without further purification. 2-Tosylaminobenzaldehyde was prepared following a method previously described [12]. The Schiff base was prepared by addition of 10 ml of a solution of freshly distilled 2-aminopyridine (0.47 g, 0.005 mol) to a solution of 2-tosylaminobenzaldehyde (1.38 g, 0.005 mol) in 50 ml of dry toluene. The mix-

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ture was heated in a Dean-Stark trap until the calculated amount of water was removed. After the reaction was completed, toluene was distilled off *in vacuo* on a water bath, and 30 ml of boiling methanol was added to the residue. The crystals precipitated upon cooling were filtered off, and washed twice with 5 ml of methanol. Recrystallized from a (1:1) methanol-benzene mixture, yielding light-yellow crystals with m.p. 112–113°. Anal: Calc. for $C_{19}H_{17}N_3O_2S: C$, 64.96; H, 4.84; N, 11.97; S, 9.12. Found: C, 64.71; H, 4.63; N, 11.89; S, 9.44.

Electrochemical synthesis

The electrochemical method used for the synthesis of the complexes was similar to that described by Tuck [13]. The cells were of the general type:

 $Pt_{(-)}/CH_3CN + HL/M_{(+)}$ M = Co, Ni, Cu, Zn or Cd

The solution was placed in a 100 ml tall form beaker, the anode was suspended into the solution by a platinum wire, and another platinum wire was used as the cathode. The ligand was dissolved in ca 50 ml of acetonitrile and a small amount of tetramethylammonium perchlorate (ca 10 mg) was added to the solution as the supporting electrolyte. **Caution!** Perchlorate salts solutions are potentially explosive. They should be handled in small quantity and with caution. As the electrolysis proceeded, hydrogen gas was evolved at the cathode. In the case of the zinc and cadmium complexes the yellow solids precipitated during the electrolysis; they were collected by filtration, washed twice with hot acetonitrile and diethylether and dried *in vacuo*. In the case of the nickel, cobalt and copper complexes, concentration of the reaction mixture by evaporation at room temperature was required to obtain solid products, which were purified as before. The crystals of $[CoL_2]$ obtained were suitable for X-ray diffraction studies. Details of the solution composition and the electrochemical conditions are given in Table 1.

Crystal structure determination

A yellow prismatic crystal of approximate dimensions $0.45 \times 0.20 \times 0.05$ mm was mounted on a glass fiber and used for data collection on a Nicolet P3 diffractometer. The monoclinic space group $P2_{1/c}$ was assumed due to extinctions observed. Data were collected at 293 K using Cu–K_a radiation ($\lambda = 1.54178$ Å) and the $\omega/2\theta$ scan technique. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. The crystal data and a summary of the data collection and structure refinement for the compound are given in Table 2.

The structure was solved by direct methods [14] and refined on F^2 by full-matrix least squares method with unit weight and anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were

Table 1. Experimental conditions for the electrochemical synthesis

Compound	Amount of $H_2L_2(g)^a$	Initial Voltage (V) ^b	Time (h)	Metal dissolved (mg)	$\frac{E_{\rm f}}{({\rm mol}~{\rm F}^{-1})}$
[CoL ₂]	0.20	15	4	88	0.51
$[NiL_2]$	0.17	25	4	96	0.53
[CuL ₂]	0.25	15	2	96	1.00
[ZnL ₂]	0.21	20	4	102	0.52
$[CdL_2]$	0.25	20	4	145	0.48

"Plus [NMe₄] ClO₄ (ca 10 mg).

^b Voltage to produce a current of 20 mA.

Formula	$C_{38}H_{32}CoN_6O_4S_2$
FW	759.75
Crystal system	Monoclinic
Space group	$P2_{1}/c$
a (Å)	11.668(3)
b (Å)	20.480(4)
c (Å)	30.075(7)
β (°)	100.85(2)
$V(Å^3)$	7058(3)
Ζ	8
$D_{\text{calc}} (\text{g cm}^{-3})$	1.430
F(000)	3144
Reflections collected	5299
Independent reflections (R _{int})	5299 (0.000)
No. of parameters	920
$\mu (mm^{-1})$	5.331
R	0.1146
Rw	0.2919

Table 2. Summary of crystal data for [CoL₂]

located from geometrical considerations (C—H = 0.95 Å), and added to the structure factor calculations as fixed contributions ($B_{iso} = 4.0 \text{ Å}^2$) and their positional parameters were not refined. The maximum difference density at final cycle 0.733; minimum -0.805. The crystal was strongly twinned, we managed to extract a correct lattice. That is the reason for the rather high *R*-factor and esd values. Two independent molecules differ in the region of p-tolyl-sulfonyl groups, one molecule has pseudosymmetry C₂, another is unsymmetrical.

Atomic scattering factors from International Tables for X-ray Crystallography [15]. Computations were performed on a DECMicroVAX 3500 computer. Atom positions, bond lengths and bond angles have been deposited as supplementary material.

RESULTS AND DISCUSSION

The anodic oxidation of the metal in an electrochemical cell containing a solution of the ligand LH in acetonitrile allows the isolation of compounds of composition $[ML_2]$, where L is the anion resulting of the deprotonation of the amide group of Schiff base.

For the cobalt, nickel, zinc and cadmium complexes, the electrochemical efficiency, defined as moles of metal dissolved per Faraday of charge, E_{f} , was close to 0.5 mol.F⁻¹, which is compatible with the following reaction scheme

Cathode:
$$2HL + 2e^- \rightarrow H_{2(g)} + 2L^-$$

Anode: $2L^- + M \rightarrow [ML_2] + 2e^-$
 $M = Co, Ni, Zn \text{ or } Cd$

For copper, $E_{\rm f}$, was close to 1 mol.F⁻¹. This value

shows that the anodic oxidation leads initially to Cu(I) species followed by further oxidation in solution to Cu(II).

Cathode:
$$HL + e^- \rightarrow 1/2H_{2(g)} + L^-$$

Anode: $L^- + Cu \rightarrow [CuL] + e^-$
 $[CuL] + HL \rightarrow 1/2H_{2(g)} + [CuL_2]$

The products obtained were characterized analitically and by IR, and NMR spectroscopies. The crystal structure of $[CoL_2]$ has been determined by Xray diffraction.

Structure of [CoL₂]

The unit cell contains two crystallographically distinct but chemically equivalent molecules (molecules A and B). Figure 1 shows the structure of molecule A with the atom numbering system used. Selected bond distances and angles for both molecules are listed in Tables 4 and 5, respectively.

The complex consists of mononuclear units with a tetracoordinate cobalt atom bound to the nitrogen atoms of two bidentate monoanionic ligands. However, the two molecules A and B are slightly different and show some variation in bond distances and angles. Thus, A has N--Co--N angles in the range $93.6(5)-123.2(5)^{\circ}$ and distances Co--N 1.981(13)-2.031(11) Å; in B the range of N--Co--N angles is 93.3(6)-131.9(6) and that of distances Co--N are 1.958(13)-1.999(13) Å. The tetrahedral environment of the cobalt atom is distorted due to the small bite required by N--Co--N = $93.0(6)-93.6(6)^{\circ}$, which also results in secondary deviation of the other perinuclear angles from the ideal values of 109° .

The Co— N_{imine} bond lengths [1.981(13), 2.000(12) Å] in A and [1.999(13) Å] in B are very similar between them, but they are shorter than the value found in another complex containing tetrahedral cobalt(II) and a Schiff base; for example, 2.066(8) Å in bis(tertbutylpyrrole-2-carboxaldimino)cobalt(II) [16]. However, the Co— N_{amide} bond lengths are substantially different in both molecules. Thus, whereas in the symmetric molecule B the Co— N_{amide} distance is 1.959(13) Å, in A those distances [1.982(12) and 2.031(11) Å] are different and larger than that of B.

The C—N bond length is in agreement with the value of 1.30 Å proposed for a C—N bond [17] and the pyridine nitrogen atom is not coordinated to the cobalt.

Spectroscopic and magnetic data

The v(N-H) broad band of the free Schiff base in the 2800-3000 cm⁻¹ region, characteristic of NH groups involved in intramolecular hydrogen bonds NH ··· N=C, is absent from the IR spectra of the complexes, consistent with the coordination of the



Fig. 1. The molecular structure of [CoL₂].

Compound	Colour	m.p.	%C	%Н	%N	%S
HL	Yellow	112	64.71(64.96)	4.63(4.84)	11.89(11.97)	9.44(9.12)
[CoL ₂]	Brown	176	59.57(60.07)	4.21(4.25)	11.12(11.06)	7.69(8.44)
[NiL ₂]	Brown	193	59.72(60.09)	4.06(4.25)	10.76(11.06)	7.69(8.44)
[CuL ₂]	Brown	165	59.11(59.71)	3.74(4.22)	10.78(10.99)	8.54(8.39)
$[ZnL_2]$	Yellow	>250	58.64(59.57)	4.04(4.21)	10.64(10.97)	7.64(8.35)
[CdL ₂]	Yellow	> 250	55.59(56.12)	3.71(3.97)	10.20(10.33)	7.23(7.87)

Table 3. Analytical data for the complexes (%)"

" Calculated values in parentheses.

deprotonated ligand. The band attributable to v(C=N) shifts to lower frequencies in all the complexes as a consequence of coordination through the imine nitrogen. On the other hand, the pyridine ring stretching band observed between 1600 and 1400 cm⁻¹ and the ring deformation bands which appear at about 600 and 400 cm⁻¹ are shifted to higher frequencies in the complexes. This behaviour has been proposed as a probe of pyridine nitrogen atom coordination to the metal. However, the structural data for $[CoL_2]$ show that the pyridine is not bound to the metal. We believe that the observed shift can be due to the change in the

conjugation between the heterocyclic ring and the rest of the ligand as a result of the coordination of the imine nitrogen to the metal. This behaviour has been previously observed in other similar systems. Therefore, these results show that the Schiff base coordinates through the imine and amide nitrogen atoms in all complexes, with a coordination number of four for the metals, in agreement with the structure of $[CoL_2]$ elucidated by X-ray diffraction.

The proton NMR data of the zinc and cadmium complexes are in accord with the above conclusions. The spectrum of the free ligand shows a peak at 12.5

Co(1)N(2)	1.981(13)	S(1C)—O(2C)	1.441(12)	
Co(1) - N(3A)	1.982(12)	S(1C) - N(3C)	1.651(14)	
Co(1)—N(2A)	2.000(12)	S(1C)—C(13C)	1.74(2)	
Co(1)—N(3)	2.031(11)	N(1)—C(10)	1.35(3)	
Co(2)—N(3B)	1.958(13)	N(1)-C(8)	1.36(2)	
Co(2)—N(3C)	1.959(11)	N(2)—C(7)	1.30(2)	
Co(2)—N(2B)	1.999(13)	N(2)—C(8)	1.40(2)	
Co(2)—N(2C)	1.999(13)	N(3) - C(1)	1.42(2)	
S(1)—O(2)	1.454(12)	N(1A)C(8A)	1.34(2)	
S(1)—O(1)	1.462(11)	N(1A)-C(10A)	1.41(2)	
S(1) - N(3)	1.578(13)	N(2A)—C(7A)	1.33(2)	
S(1) - C(13)	1.79(2)	N(2A)-C(8A)	1.44(2)	
S(1A) - O(2A)	1.471(12)	N(3A) - C(1A)	1.46(2)	
S(1A) - O(1A)	1.496(11)	N(1B)C(12B)	1.32(2)	
S(1A) - N(3A)	1.606(14)	N(1B)—C(8B)	1.34(2)	
S(1A) - C(13A)	1.75(2)	N(2B)—C(7B)	1.28(2)	
S(1B)—O(2B)	1.429(14)	N(2B)—C(8B)	1.42(2)	
$S(1B) \rightarrow O(1B)$	1.439(12)	N(3B) - C(1B)	1.43(2)	
S(1B)N(3B)	1.613(13)	N(1C)—C(8C)	1.31(2)	
S(1B) - C(13B)	1.78(2)	N(1C)—C(12C)	1.34(3)	
S(1C)—O(1C)	1.435(12)	N(2C)—C(7C)	1.30(2)	
N(2C)—C(8C)	1.41(2)	N(3C)—C(1C)	1.40(2)	
				-

Table 4. Selected bond lengths (Å) for $[CoL_2]$

Table 5. Selected bond angles (deg) for [CoL₂]

N(2)—Co(1)—N(3A)	120.4(6)	O(2A)—S(1A)—C(13A)	107.5(7)
N(2) - Co(1) - N(2A)	114.1(5)	O(1A)— $S(1A)$ — $C(13A)$	108.0(7)
N(3A)Co(1)N(2A)	93.6(6)	N(3A)— $S(1A)$ — $C(13A)$	106.7(8)
N(2) - Co(1) - N(3)	93.6(5)	O(2B)— $S(1B)$ — $O(1B)$	117.5(8)
N(3A) - Co(1) - N(3)	123.2(5)	O(2B) - S(1B) - N(3B)	114.6(8)
N(2A) - Co(1) - N(3)	113.5(5)	O(1B) - S(1B) - N(3B)	102.3(7)
N(3B)—Co(2)—N(3C)	119.1(5)	O(2B) - S(1B) - C(13B)	105.5(10)
N(3B)Co(2)N(2B)	93.3(6)	O(1B) - S(1B) - C(13B)	110.0(9)
N(3C) - Co(2) - N(2B)	119.0(5)	N(3B) - S(1B) - C(13B)	106.5(8)
N(3B)Co(2)N(2C)	131.9(6)	O(1C)— $S(1C)$ — $O(2C)$	118.4(8)
N(3C) - Co(2) - N(2C)	93.0(6)	O(1C)— $S(1C)$ — $N(3C)$	104.5(7)
N(2B)— $Co(2)$ — $N(2C)$	101.4(6)	O(2C)— $S(1C)$ — $N(3C)$	111.4(7)
O(2) - S(1) - O(1)	114.9(7)	O(1C)— $S(1C)$ — $C(13C)$	107.4(8)
O(2) - S(1) - N(3)	114.0(7)	O(2C)—S(1C)—C(13C)	108.3(9)
O(1) - S(1) - N(3)	104.0(6)	N(3C) - S(1C) - C(13C)	106.1(8)
O(2) - S(1) - C(13)	106.4(8)	C(10) - N(1) - C(8)	119(2)
O(1) - S(1) - C(13)	108.1(7)	C(7)—N(2)—C(8)	117.3(14)
N(3) - S(1) - C(13)	109.3(8)	C(7) - N(2) - Co(1)	127.4(11)
O(2A)— $S(1A)$ — $O(1A)$	116.9(7)	C(8) - N(2) - Co(1)	115.2(11)
O(2A)— $S(1A)$ — $N(3A)$	114.4(7)	C(1) - N(3) - S(1)	121.2(10)
O(1A) - S(1A) - N(3A)	102.9(6)	C(1) - N(3) - Co(1)	125.5(10)
S(1) - N(3) - Co(1)	112.9(7)		

ppm, assignable to the amide hydrogen, which is absent in the spectra of the complexes. The peak for the imine hydrogen atom (9.3 ppm in the free ligand) undergoes a shift towards higher field in the compounds, 9.1 ppm, and the peak for the 6-hydrogen of the pyridine ring is practically at the same field in the spectra of complexes and free ligand.

The solid state electronic spectrum in the near IR-

visible region of the cobalt(II) complex, shows two *dd* transition bands, one at 16,800–18,800 cm⁻¹ and the other in the range 6600–8400 cm⁻¹; of the type expected for distorted tetrahedral cobalt(II) compounds [18]. The band in the visible region has been assigned to a ${}^{4}T_{1}(P) \leftarrow {}^{4}A_{2}$ (v_{3}) transition, and the multicomponent one in the near IR region to ${}^{4}T_{1}(F) \leftarrow {}^{4}A_{2}$ (v_{2}) transition. The ${}^{4}T_{2} \leftarrow {}^{4}A_{2}$ (v_{1}) transition has not been observed, but its position at ca 4520 cm^{-1} has been calculated as described by Lever. The values obtained for 10 Dq (4520 cm^{-1}), β (0.83) and B (804 cm^{-1}) are also in the range expected for pseudotetrahedral cobalt(II) complexes. The magnetic moment for this complex is 4.65 B.M. is in the range expected for tetrahedral cobalt(II) compounds.

The value of the magnetic moment of the copper complex (1.8 B.M.) corresponds to one unpaired electron. The solid state electronic spectrum shows two bands at around 10,700 and 18,100 cm⁻¹, and is consistent with an approximately square-planar stereochemistry. The band that appears at 27,000 cm⁻¹ may be assigned to a charge transfer transition. The magnetic moment of the nickel(II) complex (3.18 B.M.) and its solid reflectance spectrum are consistent with a tetrahedral geometry for the complex. The bands observed at ca 8200 and 14,200 cm⁻¹ are assigned to the two highest of the three expected spin allowed transitions, ${}^{3}A_{2} \leftarrow {}^{3}T_{1}$ (v_{2}) and ${}^{3}T_{1}(P) \leftarrow {}^{3}T_{1}(F)$ (v_{3}), respectively.

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