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Electrochemical Synthesis of Zinc and Cadmium Complexes with *N*-[(2-pyrrolyl)methylidyne]-*N'*-tosylbenzene-1,2-diamine. The Crystal Structure of Bis-{*N*-[(2-pyrrolyl)methylidyne]-*N'*-tosylbenzene-1,2-diaminato}zinc(II)

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Electrochemical oxidation of zinc and cadmium in a solution of *N*-[(2-pyrrolyl)methylidyne]-*N'*-tosylbenzene-1,2-diamine, H_2L, in acetonitrile afforded the compounds $[M(HL)_2]$, M=Zn, Cd. The crystal structure of bis-{*N*-[(2-pyrrolyl)methylidyne]-*N'*-tosylbenzene-1,2-diaminato}zinc(II) has been determined by X-ray diffraction. The structure consists of monomeric molecules with the zinc atom in a distorted tetrahedral geometry. The IR and ^1H NMR spectra of the complexes are discussed and related to their structures.

The application of an electrolytic procedure for the preparation of metal complexes has been widely developed by Tuck.[1] We have used this electrochemical approach for the synthesis of metallic complexes with weak acid Schiff bases ligands in which the acid group is usually a hydroxyl[2–7] or a pyrrolic NH group.[8–11]

As a continuation of this work, we have now carried out the electrochemical synthesis of Zn and Cd complexes with *N*-[(2-pyrrolyl)methylidyne]-*N'*-tosylbenzene-1,2-diamine (H_2L), a Schiff base ligand containing two N–H weak acid groups.

Experimental

Acetonitrile and 2-aldehyde pyrrol were comercial products, and were used without further purification. Zinc and cadmium were used as plates (ca. 2×2 cm^2). *N*-Tosyl-1,2-diaminobenzene was obtained following the method described by Malick.[12] The Schiff *N*-[(2-pyrrolyl)methylidyne]-*N'*-tosylbenzene-1,2-diamine (H_2L), Fig. 1, was isolated from the condensation of *N*-tosyl-1,2-diaminobenzene and 2-aldehyde pyrrole in methanol. Its purity was checked by elemental analysis and by recording its ^1H NMR spectrum. Anal. Found: C, 63.4, H, 4.9; N, 12.5; S, 9.5. Calculated for $[C_{18}H_{17}N_3O_2S)]$: C, 63.7, H, 5.0; N, 12.4; S, 9.4. ^1H NMR (DMSO-d_6; ppm): 11.9 ($N-H_{pyr}$, s, 1H), 9.3 ($N-H_{tosyl}$, s, 1H), 8.2 (CH=N, s, 1H).

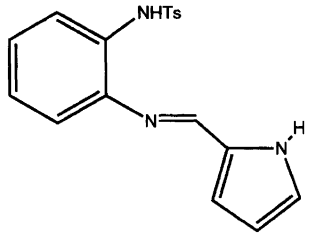

Fig. 1. Scheme of the Schiff base.

Electrochemical synthesis. The electrochemical procedure used in the synthesis of complexes was similar to that described by Tuck.[13] The cell was a tall-form beaker with a rubber bung through which the electrochemical leads entered into the cell. The metallic anode was suspended from a platinum wire in a solution of the corresponding ligand in acetonitrile. Another platinum

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wire was the cathode. Direct current was obtained from a purpose-built d.c. power supply. The cell can be summarized as:

$Pt_{(-)}/MeCN + H_2L/M_{(+)}$ $M = Zn, Cd$

[Zn(HL)$_2$]. Electrolysis of an acetonitrile solution (50 cm^3) containing H_2L (0.25 g, 7.35 mmol) and a small amount of tetramethylammonium perchlorate (ca. 10 mg), at 20 V and 10 mA for 4 h dissolved 48 mg of zinc ($E_f = 0.98$). At the end of the experiment the yellow crystalline solid was filtered, washed with hot acetonitrile and ether, and dried *in vacuo*. The compound was characterized as [Zn(HL)$_2$] by elemental analysis. Anal. Found: C, 58.1, H, 4.4; N, 11.4; S, 8.4. Calculated for [$C_{36}H_{32}N_6O_4S_2Zn$]: C, 58.5, H, 4.1; N, 11.4; S, 8.7%.

[Cd(HL)$_2$]. The electrochemical oxidation of cadmium in an acetonitrile solution (50 cm^3) containing the ligand H_2L (0.25 g, 7.35 mmol) using a 10 mA current for 4 h resulted in the dissolution of 92 mg of the metal (E_f = 1.08). At the end of the electrolysis the yellow solid was filtered, washed with acetonitrile and ether and dried *in vacuo*. Anal. Found: C, 54.4; H, 4.1; N, 10.7; S, 8.0. Calculated for [$C_{36}H_{32}N_6O_4S_2Cd$]: C, 55.0; H, 4.1; N, 10.7; S, 8.1%.

Physical measurements. Microanalyses were performed on a Carlo-Erba EA 1108 microanalyzer. IR spectra were recorded in KBr mulls on a Perkin Elmer 180 spectrophotometer. NMR spectra were recorded in a Bruker AMX 300 MHz spectrometer, using DMSO-d_6 as solvent. Chemical shifts were determined against TMS as internal standard.

Crystal structure determination.

X-Ray data collection and processing. Intensity data for a yellow prismatic crystal with dimensions $0.10 \times 0.15 \times 0.30$ mm were measured at room temperature on an Enraf-Nonius CAD4 diffractometer fitted with graphite-monochromatised Mo$K\alpha$ radiation, (λ = 0.710 73 Å). Cell parameters were refined by a least-squares procedure on the setting angles of 25 reflections ($6.7 < \theta < 13.5°$).[14] The $\omega/2\theta$ scan tecnique was employed to measure the intensities up to a maximun Bragg angle of 29°. No decomposition of the crystal ocurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absortion (μ = 0.88 mm^{-1}).[15] A total of 10 039 reflections were collected, of which 9311 were unique ($R_{int} = 0.032$), and of these 2034 satisfied the $I > 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Structure solution and refinement. The structure was solved by direct methods[16] and refined by a full-matrix least-squares procedure based on F.[14] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from difference Fourier synthesis and added to the structure factor calculations with fixed isotropic B-values ($B_{eq} = 4.0$ Å^2), but their positions were not refined. A weighting scheme of the form $w = 1/\sigma^2(F)$ was introduced and the refinement proceeded smoothly to convergence with a maximun Δ/σ of 0.001 when $R = 0.053$, $R_w = 0.057$ and GOF = 3.52 (goodness-of-fit) for 223 variables. Correction for extinction was made in the last cycle of refinement.[17] The secondary extinction coefficient refined to $g = 5.926 \times 10^{-8}\{F_c = F_c/[1 + g(F_c)^2 Lp]\}$. The analysis of variance showed no special features, and the maximum and minimum residual electron density peaks in the final difference map were 0.45 and -0.45 e Å^{-3}, respectively. Programs used were SHELXS-86[16] and ORTEPII,[18] atomic scattering factors and anomalous dispersion corrections for all atoms were taken of from Ref. 19. The atomic positions, full lists of bond lengths and angles and other crystallographic data have been deposited as Supplementary Publication No. CSD 406323. Copies can be obtained through the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen. Germany.

Results and discussion

The anodic oxidation of zinc or cadmiun in the presence of *N*-[(2-pyrrolyl)methylidyne]-*N'*-tosylbenzene (H_2L) is a simple, efficient route to [Zn(HL)$_2$] or [Cd(HL)$_2$]. In both cases the product formed was easily separated by filtration from the bottom of the cell as a yellow crystalline product. These compounds are insoluble in common organic solvents, and have melting points up to 250 °C. In the case of the zinc compound the crystals obtained in the cell were suitable for X-ray studies.

The values of the electrochemical efficiency, defined as the amount of metal dissolved per unit of charge (in F), were, in both cases, close to 0.5. This fact and the evolution of hydrogen from the cathode are compatible with the following mechanism:

cathode: $2H_2L + 2e^- \rightarrow 2HL^- + H_2$

anode : $M(Zn,Cd) \rightarrow M^{+2} + 2e^-$

Structure of [Zn(HL)$_2$]. The molecular structure of [Zn(HL)$_2$], with the atom labelling, is illustrated in Fig. 2. Final atomic coordinates are given in Table 2, and bond lengths and angles, with estimated standard deviations, in Tables 3 and 4, respectively. The zinc atom is located on a crystallographic two-fold axis and is coordinated to the amide and imine nitrogen of two symmetry related moities. The pyrrolic nitrogen atoms of the Schiff bases are not coordinated to the metal. The coordination polyhedron around the zinc atom is distorted tetrahedral. This distortion is caused mainly by the small bite angle, 83.4(3)°, of the bidentated Schiff-base ligand, and the other bond angles around the zinc atom are in the range 118.5(2)–127.2(3)°. Two different Zn–N bond distances are observed; the bonds involving amide nitrogen atoms, 1.962(5) Å, are significantly shorter than those involving imino nitrogen atoms, 2.049(4) Å. These values are similar to those found in other tetrahedral compounds of zinc containing both

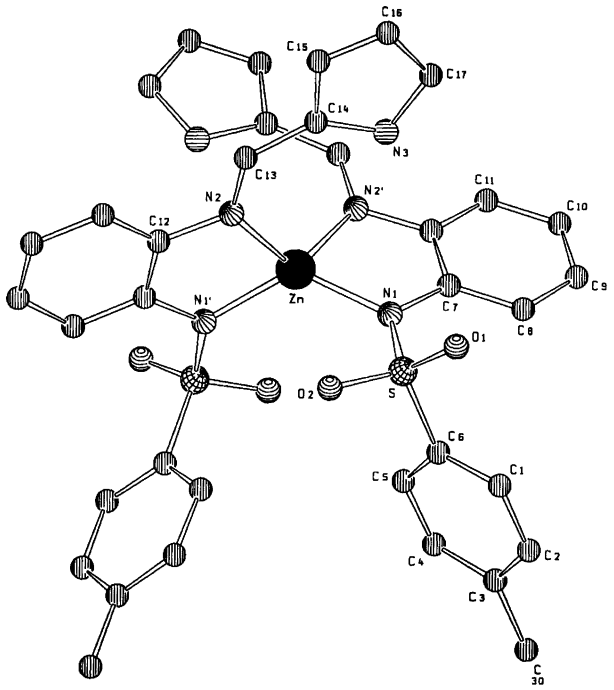

Fig. 2. Perspective view for $[Zn(HL)_2]$.

Table 1. Summary of crystal data.

Formula	$C_{36}H_{32}N_6O_4S_2Zn$
M	742.19
Crystal system	Monoclinic
Space group	*C2/c*
a/Å	21.811(7)
b/Å	11.523(2)
c/Å	14.063(4)
β/°	98.64(2)
V/Å^3	3494(2)
Z	4
Density(calc.)/g cm^{-3}	1.411
F(000)	1536
Radiation	Mo*K*α
μ/mm^{-1}	0.88
Wavelength/Å	0.71073
Total no. of refl. measured	10039
No.of observed refl. criterion	2034[$I>3\sigma(I)$]
No. of unique refl. (R_{int})	9311(0.032)
R	0.053
R_w	0.057
GOF	3.52

Table 2. Positional parameters for $[Zn(HL)_2]$ and their estimated standard deviations in parentheses.

Atom	*x*	*y*	*z*	*B*/Å^2
Zn	0.500	0.09262(9)	0.750	2.73(2)
S	0.40184(7)	0.2598(1)	0.8189(1)	3.28(3)
O(1)	0.3501(2)	0.2238(4)	0.8644(3)	4.4(1)
O(2)	0.4596(2)	0.2817(4)	0.8816(3)	4.4(1)
N(1)	0.4189(2)	0.1684(4)	0.7421(3)	3.1(1)
N(2)	0.5428(2)	0.0016(4)	0.8666(3)	2.60(9)
N(3)	0.4089(3)	−0.1189(6)	0.8345(4)	5.8(2)
C(1)	0.3262(3)	0.4462(5)	0.7704(4)	3.5(1)
C(2)	0.3087(3)	0.5471(6)	0.7193(5)	4.3(1)
C(3)	0.3435(3)	0.5931(6)	0.6541(4)	4.1(1)
C(4)	0.3962(3)	0.5332(7)	0.6409(5)	5.1(2)
C(5)	0.4149(3)	0.4330(6)	0.6904(5)	4.6(2)
C(6)	0.3795(3)	0.3892(5)	0.7558(4)	3.2(1)
C(7)	0.3749(2)	0.1272(5)	0.6663(4)	2.9(1)
C(8)	0.3133(3)	0.1662(6)	0.6454(5)	3.6(1)
C(9)	0.2732(3)	0.1213(6)	0.5685(5)	4.1(1)
C(10)	0.2930(3)	0.0366(6)	0.5124(5)	4.3(1)
C(11)	0.3530(3)	−0.0038(5)	0.5309(4)	3.5(1)
C(12)	0.6054(2)	0.0395(5)	0.8918(4)	2.7(1)
C(13)	0.5235(3)	−0.0856(6)	0.9123(4)	3.2(1)
C(14)	0.4635(3)	−0.1375(5)	0.8970(4)	3.1(1)
C(15)	0.4534(2)	−0.2319(5)	0.9515(4)	2.9(1)
C(16)	0.3960(3)	−0.2711(7)	0.9266(5)	5.0(2)
C(17)	0.3668(3)	−0.2041(6)	0.8534(5)	4.6(2)
C(30)	0.3240(5)	0.7025(7)	0.6011(6)	6.8(2)

Table 3. Select bond distances (in Å) for $[Zn(HL)_2]$ with e.s.d.s in parentheses.

Zn–N(1)	1.962(3)	N(1)–C(7)	1.405(7)
Zn–N(2)	2.049(4)	N(2)–C(12)	1.425(7)
S–O(1)	1.440(5)	N(2)–C(13)	1.298(8)
S–O(2)	1.447(4)	N(3)–C(14)	1.386(8)
S–N(1)	1.592(6)	N(3)–C(17)	1.40(1)
S–C(6)	1.766(6)		

Table 4. Select bond angles (in °) for $Zn(HL)_2$ with e.s.d.s in parentheses.

N(1)–Zn–N(1′)	127.2(3)	O(2)–S–C(6)	107.9(3)
N(1)–Zn–N(2)	124.9(2)	N(1)–S–C(6)	107.0(3)
N(1)–Zn–N(2′)	83.4(2)	S–N(1)–C(7)	122.4(4)
N(2)–Zn–N(2′)	118.5(2)	C(12)–N(2)–C(13)	119.0(4)
O(1)–S–O(2)	116.5(2)	N(1)–C(7)–C(12)	116.8(5)
O(1)–S–N(1)	112.9(3)	N(2)–C(12)–C(7)	116.1(4)
O(1)–S–C(6)	106.9(3)	N(2)–C(13)–C(14)	127.6(5)

anionic and neutral nitrogen donor atoms, e.g. 1.962(2), 1.971(2) Å and 2.023(2), 2.041(2) Å in bis{*N*-[1-(2-pyrrolyl)ethylidene]ethylaminato}Zn(II)[20] with Zn-N bonds involving anionic pyrrolate nitrogen atoms and ethylamino atoms or in Zn(pyrrole-2-CH=N-But)$_2$ with 1.975(2) and 2.067(2) Å for Zn–N(pyrrole) and Zn–N(imine),[21] respectively. Each five-membered chelate ring lies in a plane, the maximun deviation of any atom being 0.004 Å. Both planes are nearly perpendicular, with a dihedral angle of 87.8°.

In each ligand the phenyl and pyrrole rings are planar. Bond lengths and angles within the Schiff base are as expected. In particular, the imine C–N bond length, 1.298(8) Å, is in agreement with the value of 1.30 Å proposed for a C=N bond.[22]

Spectroscopic studies. The IR spectra of the complexes are consistent with the X-ray data discussed above. The ligand H_2L shows two bands at 3352 and 3230 cm^{-1} attributable to $\nu(N–H)_{pyrrole}$ and $\nu(N–H)_{tosyl}$, respectively. In the IR spectrum of the zinc complex the band of the free ligand at 3352 cm^{-1} is absent; only one band is seen above 3000 cm^{-1} at 3257 cm^{-1}. This is in accordance with the deprotonation of the amide N–H bond

and the keeping of the pyrrole group intact. On the other hand, the free ligand shows a band at 1618 cm^{-1}, which in the case of the zinc complex appears at 1608 cm^{-1}. This shift to lower frequency can be interpreted as a result of the coordination of the imine nitrogen to the metal.[23] In the case of the cadmium complex, the pertinent data are 3261 and 1604 cm^{-1}. This shows that this complex has a tetrahedral geometry around the cadmium atom, with the ligand using the amide and imine nitrogen atoms, but with a free pyrrole nitrogen group.

The ^1H NMR spectra of the complexes reinforce the above conclusion. The spectrum of the ligand shows two singlets at 11.9 and 9.3 pmm asignable to the pyrrole and amide proton, respectively. Both signals disappear by deuteration. A signal at 8.2 ppm is assigned to the imine proton and the multiplet at 7.6–6.2 ppm to the aromatic hydrogens. The spectra of both complexes show that the signal due to the amide proton dissapears, showing that this group has been deprotonised. The signal of the imine group is shifted downfield, 8.7 and 9.2 for $[Zn(HL)_2]$ and $[Cd(HL)_2]$, respectively. This is in agreement with coordination of the ligand through this group. The signal of the pyrrole hydrogen remains unaffected.

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