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Electrochemical Synthesis and Characterization of Zinc(II) and Cadmium(II) Complexes of Dianionic Tetradentate Schiff Base Ligand

Laura Rodríguez, Elena Labisbal, Antonio Sousa-Pedrares, Jaime Romero, José-Arturo García Vázquez*, and Antonio Sousa

Santiago de Compostela/Spain, Departamento de Química Inorgánica, Universidad de Santiago de Compostela

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 65th Birthday

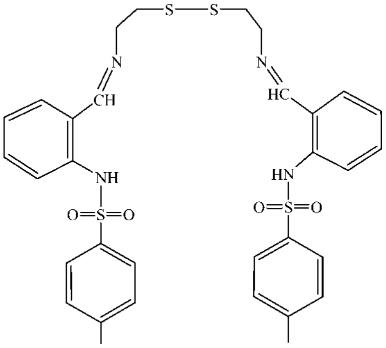
Abstract. The electrochemical oxidation of anodic metal (zinc or cadmium) in acetonitrile solution of the potentially chelating Schiff base *N,N*-(dithiodiethylenebis(aminylydenemethylydene)-bis(1,2-phenylene)ditosylamide (H_2L) afforded stable complexes of empirical formula [ML]. The crystal and molecular structures of $[ZnL]\cdot CH_3CN$ (**1**) and [CdL] (**2**) have been determined by X-ray diffraction. In both complexes the metal atom is in a distorted tetrahedral environment with the Schiff base acting as a tetradentate N_4 donor. Spectroscopic data for the complexes (IR, ES MS and ^1H NMR spectra) are discussed and related to the structural information.

Keywords: Electrochemical synthesis; Schiff base complexes; Sulfonamide complexes; Zinc; Cadmium; Crystal structure

1 Introduction

Considerable attention has been paid to *N*-donor metal complexes in view of their interesting chemical properties and potentially useful biochemical applications [1−3]. Of particular interest are complexes of Schiff bases having NNS donor sequences, owing to the industrial, carcinostatic, antitumour, antiviral and antimalarial activity of the complexes derived from these ligands [4−7]. However, the synthesis of free Schiff base proligands containing thiol groups can be problematic due to the formation of thiazolines [8]. In order to overcome these difficulties, an electrochemical reductive cleavage of a disulfide bond present in the preformed Schiff base has been used and the electrochemical synthesis and structural characterization of zinc and cadmium complexes of the dianionic terdentate 2-mercaptophenyliminophenolato ligand have been reported [9, 10]. However, in some cases the reductive cleavage of the S−S bond did not occur [11].

As part of our continuing interest in the coordination chemistry of Schiff base ligands, we describe here the synthesis and characterization of zinc and cadmium complexes with the Schiff base derivative of bis(2-aminoethyl)disulfide with 2-tosylaminobenzaldehyde a ligand characterized by the presence of imine and amide donor groups (Scheme 1).



Scheme 1

Although the difficulty in replacing the amide hydrogen atom by a metal atom is well known [12], the electron-withdrawing effect of the sulfonyl group increases the acidity of the N−H group and, in the deprotonated form, these anionic systems are effective sigma-donor ligands. The coordination process is facilitated by the presence of the additional imine nitrogen donor atom on the ligand, allowing the formation of stable six-membered chelate rings with the metal ion. In this way, metal complexes of sulfonamide ligands incorporating additional donor atoms from iminomethyl and phenol groups [13], iminomethyl and thiophenol groups [14] or pyridine groups [15−18] have been investigated.

2 Results and Discussion

The condensation of bis(2-aminoethyl)disulfide with 2-tosylaminobenzaldehyde in a 1:2 ratio yielded the Schiff base H_2L, in good yield (see Experimental part).

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* Profesor Dr. José Arturo García Vázquez
Departamento de Química Inorgánica
Universidad de Santiago de Compostela
E-15782-Santiago de Compostela
E-mail: qijagv@usc.es
FAX: +34-981547102

The anodic oxidation of zinc, or cadmium, in the presence of H_2L is a direct and efficient route to obtain complexes for which the elemental analyses indicate that the ligand reacts with the metals to afford the neutral complexes [ZnL] or [CdL], where L represents the bi-deprotonated form of the ligand, without reductive cleavage of the S−S bond. This is supported by molar conductivity measurements of the complexes in 10^{-3} M DMF solutions which are in the close to 10 Ω^{-1} cm^2 mol^{-1} [19].

The metal compounds are moderately soluble in the reaction medium and they are obtained as crystalline air-stable solids at the bottom of the cell. The complexes are insoluble in non-polar solvents, moderately soluble in chloroform and soluble in polar solvents such as dimethylsulfoxide or *N,N*-dimethylformamide. Crystallization from the mother liquor afforded crystals of [ZnL].CH_3CN and [CdL] suitable for X-ray studies.

The electrochemical efficiency (see Experimental part), defined as the amount of metal dissolved per Faraday of charge, were in all cases close to 0.5 mol.F^{-1}. This, and the formation of hydrogen at the cathode, is consistent with the following reaction schemes:

Cathode: $H_2L + 2e^- \longrightarrow L^{2-} + H_2$
Anode: $M \longrightarrow M^{2+} + 2e^-$
Overall: $H_2L + M \longrightarrow [ML] + H_2$
M = Zn, Cd.

2.1 The crystal structures of [ZnL]·CH_3CN and [CdL]

Crystallographic data and experimental details, refinement results and details for the structure determination are listed in Table 1. The molecular structures of [ZnL].CH_3CN and [CdL] are shown in Figures 1 and 2. Selected bond distances and angles are given in Tables 2 and 3.

Table 1 Crystal data and details of refinement for the complexes

	[ZnL].CH_3CN	**[CdL]**
Empirical formula	$C_{34}H_{35}N_5O_4S_4Zn$	$C_{32}H_{32}CdN_4O_4S_4$
Molecular mass	771.28	777.26
Temperature /K	293(2)	293(2)
Wavelength /Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
a /Å	21.714(5)	34.526(7)
b /Å	8.4350(18)	10.936(2)
c /Å	21.070(5)	17.788(3)
β /°	110.067	101.879
V /Å^3	3624.9(14)	6572(2)
Z	4	8
Absorption coefficient /mm^{-1}	0.952	0.962
Crystal size /mm	0.39 × 0.13 × 0.05	0.34 × 0.24 × 0.12
Reflections collected	7378	41494
Independent reflections	7378 [*R*(int) = 0.0000]	8028 [*R*(int) = 0.0464]
Final *R* ind [I > 2σ(I)]	*R*1 = 0.0579	*R*1 = 0.0377
All data	*wR*2 = 0.0975	*wR*2 = 0.0826

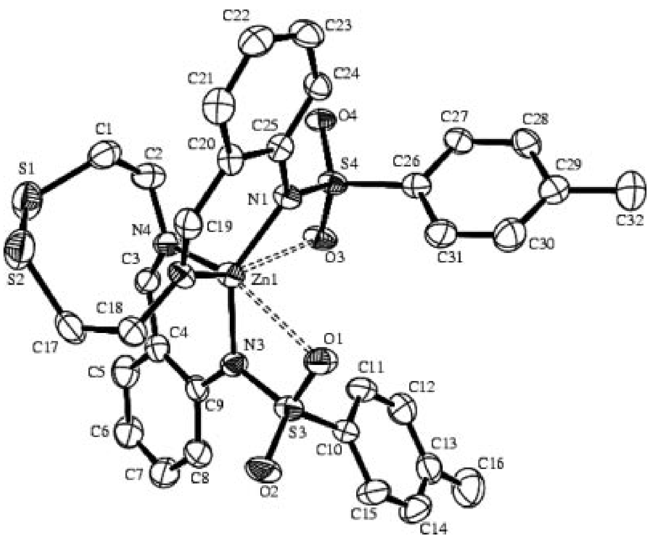

Fig. 1 Molecular structure of [ZnL].$2CH_3CN$

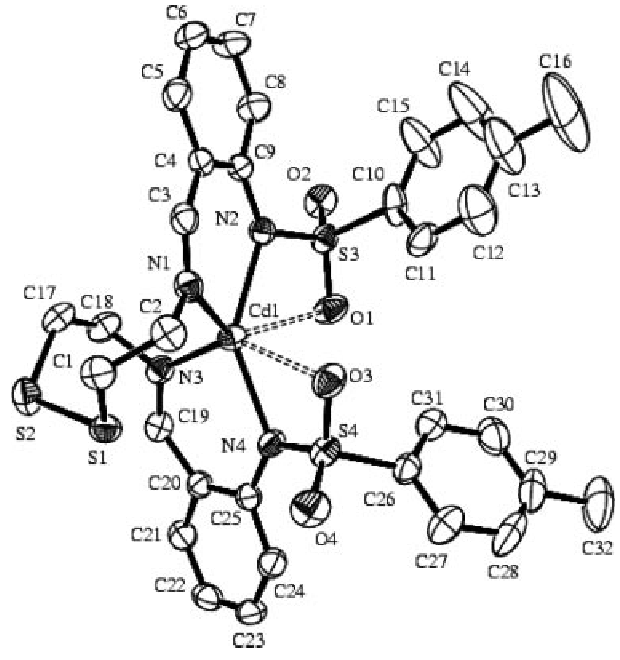

Fig. 2 Molecular structure of [CdL]

Table 2 Selected bond distances /Å and angles /deg for [ZnL].CH_3CN

Zn(1)-N(1)	1.980(4)	Zn(1)-N(4)	2.049(5)
Zn(1)-N(2)	2.033(5)	Zn(1)-O(3)	2.642(4)
Zn(1)-N(3)	1.981(5)	Zn(1)-O(1)	2.634(4)
N(2)-Zn(1)-N(1)	93.4(2)	N(4)-Zn(1)-N(2)	109.3(2)
N(4)-Zn(1)-N(3)	93.0(2)	N(2)-Zn(1)-N(3)	110.5(2)
N(4)-Zn(1)-N(1)	106.4(2)	N(3)-Zn(1)-N(1)	142.3(2)

Both compounds consist of molecular units in which the metal atom is tetracoordinated by two imine nitrogen and two amidate nitrogen atoms of a dianionic tetradentate ligand.

Table 3 Selected bond distances /Å and angles /deg for [CdL]

Cd(1)-N(4)	2.227(3)	Cd(1)-N(2)	2.239(3)
Cd(1)-N(3)	2.232(3)	Cd(1)-N(1)	2.274(3)
Cd(1)-O(3)	2.595(3)	Cd(1)-O(1)	2.652(3)
N(2)-Cd(1)-N(1)	82.41(11)	N(4)-Cd(1)-N(3)	85.40(11)
N(4)-Cd(1)-N(2)	140.77(11)	N(2)-Cd(1)-N(3)	108.11(11)
N(4)-Cd(1)-N(1)	124.55(11)	N(3)-Cd(1)-N(1)	117.62(11)

The coordination polyhedron around the metal atom is distorted tetrahedral, mainly due to the rigidity of chelate rings, with bond angles of 93.2(2)° and 83.90(11)° (average values) in [ZnL] and [CdL], respectively. The M−N bond distances in both complexes are as expected and close those to found in other complexes containing similar ligands. For example, the Zn−N(imine) bond distance 2.041(5) Å (average value) is similar to that found in bis{2-[pyrrol-2-yl)methydeneamino]thiophenolato-S,N}zinc(II), 2.057(3) Å (average value) [20], or in bis[N-(4-methylphenyl)salicylaldiminato]Zn(II), 2.007(3) Å [21]. Both of these complexes have a distorted tetrahedral coordination around the metal atom. The mean Zn−N(amide) bond distance is shorter 1.980(5) Å, but is also close to those found in other complexes containing amidate nitrogen ligands and a zinc atom in a tetrahedral environment; for instance 1.942(8) Å in {[*N*,*N*′-bis(butanesulfonamide)-1,2-diaminocyclohexane]-(2,2′-bipyridyl)}zinc(II) [22] and 1.962(3) Å in bis{*N*-[(2-pyrrolyl)methylene]-*N*′-tosylbenzene-1,2-diaminato}-zinc(II) [23]. In addition, the Cd−N(amide) bond distance, 2.229(3) Å (average value), is similar to those described in K[Cd($ClC_6H_4SO_2NCONH$-*n*-Pr)$_3$], in which the mean Cd−N(amide) bond distance is 2.21(2) Å [24] and in [Cd(bipy)$_2$(bsglyNO)$_2$] [25], mean bond distance 2.215 Å.

Weak contact between the metal atoms and the O(1) and O(3) atoms of the two sulfonyl groups are also observed in both compounds, with the M−O distances being 2.634(4) and 2.642(4) Å for [ZnL] and 2.595(3) and 2.652 Å for [CdL], in both cases shorter than the sum of the van der Waals radii (2.90 and 3.10 Å for Zn−O and Cd−O) [26]. These contacts make the N(4)−M−N(2) bond angle 142.3(2)° and 140.77(11)°, respectively, for **1** and **2** − longer than one would expect for a regular tetrahedron. If this interaction is taken into account, the metal atoms would be in an [MN_4O_2] six-coordinate environment [4+2]. Weak interactions are usually observed in zinc and cadmium complexes containing ligands with sulfonyl groups. Thus, in the zinc compound with [(4-methylphenyl)sulfonyl]-1*H*-amido-2-phenyl-2-oxazolines [27], a secondary contact between the zinc atom and an oxygen of the sulfonyl group is observed, with a Zn−O bond distance of 2.6801(14) Å − similar to that found in the compound reported here. In the same way, in bis{[(4-methylphenyl)sulfonyl]-2-pyridylamide}cadmiun(II), in addition to Cd−O(sulfonyl) bond distances of 2.335(5) Å, longer Cd−O distances of 2.738(6) Å are also observed and are indicative of a weak interaction [16].

The sulfur atoms of the disulfide fragment of the ligands are not coordinated to the metal atom. The S−S bond distance, 2.035(3) and 2.038(2) Å for the **1** and **2**, respectively, are close to those found in free disulfide ligands (2.037 Å in 2-{(*N*,*N*-dimethylamino)ethyl}disulfide [28] and 2.066 Å in 2,2′-diaminodiphenyldisulfide [29] and also similar to those found in zinc [11], manganese [30], iron [31] and nickel [32] complexes with Schiff bases derived from 2,2′-diaminodiphenyldisulfide and salicylaldehyde, with S−S bond distances in the range 2.046−2.066 Å. Other structural parameters in the ligand are as expected, with C−N bond lengths of 1.282(7) and 1.274(5) Å (average values) for **1** and **2**, respectively, in good agreement with the value of 1.30 Å proposed for a C=N bond [33]. The zinc compound crystallizes with an acetonitrile molecule that is located within the network but does not interact significantly with the complex.

2.2 *Spectroscopic studies*

Major vibration bands of the free ligands and metal complexes are given in the experimental part. The ν(NH) band was not observed in the IR spectra of any metal complex, indicating deprotonation of the ligand and coordination. In addition, the strong band in the ligand at 1630 cm^{-1}, assigned to ν(C=N), shows red shifts in the complexes. Furthermore, the ν(C−N) stretching frequency is shifted to lower wavenumbers in the complexes. This behaviour is compatible with the participation of both imine and amide nitrogen atoms in the coordination to metal atoms. Finally, two bands in the ranges 1249−1258 cm^{-1} and 1155−1158 cm^{-1} are assigned to the asymmetric and symmetric vibration modes of the SO_2 group and are close to those found in the free ligands [34, 35]. The ES mass spectra (*Experimental part*) show peaks assigned to [ML]$^+$ fragments for both complexes, indicating ligand coordination to the metal atom. Peaks assigned to [M_2L_2]$^+$ fragments could not be detected for any of the complexes, suggesting a mononuclear nature for all of these compounds in solution.

The ^1H NMR spectra of the complexes at room temperature (*Experimental part*) show the disappearance of the NH protons present in the free ligand, a situation consistent with the bis-deprotonation of the Schiff base. The imine hydrogen atom undergoes an upfield shift on complexation, indicating a withdrawal of charge from the imine group upon coordination. Therefore, these imine nitrogen atoms should be coordinated to the metal ions. The aromatic protons are slightly shifted to lower field, showing a drain of charge from the phenyl ring. The aromatic proton signals of the tosyl groups also shift on complexation. This could be attributed to some interaction between the tosyl groups and the metal atoms, as the solid-state X-ray structures of Zn and Cd complexes seem to confirm.

3 Experimental Section

Acetonitrile, aldehyde, amine and all other reagents were used without further purification. Zinc and cadmium (Ega Chemie) were used as 2 x 2 cm plates.

Preparation of the ligand H_2L.

To a vigorously stirred solution of bis(2-aminoethyl)disulfide (1 g, 6.6 mmol) in MeOH (40 mL) was added 2-tosylamidebenzaldehyde (3.6 g, 13.1 mmol). The reaction mixture was heated under reflux with a Dean−Stark condenser for 3−4 h. The precipitated product was collected by filtration, washed thoroughly with MeOH (10 mL) and dried in vacuo. 3.6 g (82 %). Anal. Calc. for $C_{32}H_{34}N_4O_4S_4$: C, 57.63; H, 5.14; N, 8.40; found C 57.30, H 4.99, N 8.66 %.

Mass spectrometry 667.1, (HL^+, 100 %). **^{1}H NMR** ($CDCl_3$, ppm): 12.9 (s, 2H, -NH), 8.4 (s, 2H, N=CH), 7.8−6.9 (m, 16H. aromatics), 3.9 (t, 4H, N-CH_2), 3.2 (t, 4H, S-CH_2), 1.6 (s, 6H, CH_3). **IR** spectroscopy (KBr, cm^{-1}): ν (NH) 3284 (m), ν (C=N) 1630 (s), ν (C-N) 1338 (s), $\nu_{as}(SO_2)$ 1285 (s), $\nu_s(SO_2)$ 1153 (s).

Electrochemical synthesis of metal complexes.

The complexes were obtained using an electrochemical procedure [36]. The cell was a 100 ml tall-form baker fitted with a rubber bung through the electrochemical leads entered. An acetonitrile solution of the ligand was electrolysed using a platinum wire as the cathode and the metal plate as the anode. Tetramethylammonium perchlorate (10 mg) was added as a supporting electrolyte. (**Caution:** *Although no problem has been encountered in this work, all perchlorate compounds are potentially explosive and should be handled in small quantities and with great care!*). Direct current was obtained from a purpose-built d.c. power supply. Applied voltages of 10−20 V allowed sufficient current flow for smooth dissolution of the metal. The cell can be summarized as:

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

[ZnL].CH_3CN. Electrochemical oxidation of a zinc anode in a solution of H_2L (60.0 mg, 0.09 mmol) in acetonitrile (70 mL) containing about 10 mg of tetramethylammonium perchlorate as supporting electrolyte for 1 h with a current of 5 mA caused 6.0 mg of zinc to be dissolved. $E_f = 0.49$ mol F^{-1}. During the electrolysis process, hydrogen was evolved at the cathode and at the end of the reaction a small quantity of an unidentified insoluble product was filtered off. The mother liquor was left to stand for one week. Slow evaporation of the solution yielded small white crystals of [ZnL].CH_3CN that were suitable for X-ray diffraction. Yield 48 mg (70 %). Anal. Calc. for $C_{34}H_{35}N_5ZnO_4S_4$: C, 52.94; H, 4.57; N, 9.08; S, 16.63; found C, 53.00; H, 4.77; N, 9.17; S, 16.88 %. IR spectroscopy (KBr, cm^{-1}): ν(C=N) xxx(x), ν(C−N) xxx(x), $\nu_{as}(SO_2)$ 1258(s), $\nu_s(SO_2)$ 1153(s).

Mass spectrometry 771 ($ML.CH_3CN^+$, 100 %). **^{1}H NMR** ($CDCl_3$, ppm): 8.2 (s, 2H, N=CH), 7.3−6.8 (m, 16H, aromatics), 3.6 (t, 4H, N-CH_2), 3.2 (t, 4H, S-CH_2), 2.4 (s, 6H, CH_3). **IR** spectroscopy (KBr, cm^{-1}): ν(C=N) 1628 (s), ν(C−N) 1286 (s), $\nu_{as}(SO_2)$ 1258 (s), $\nu_s(SO_2)$ 1155 (s)

[CdL]. H_2L (60 mg, 0.09 mmol) in acetonitrile (70 mL) was electrolysed for 1 h with a current of 5 mA for 1 h, causing 10.5 mg of metal to be dissolved. $E_f = 0.49$ mol F^{-1}. Slow evaporation of the solution yielded small white crystals of [CdL]· that were suitable for X-ray diffraction. Yield 42 mg (60 %). Anal. Calc. for $C_{32}H_{32}CdN_4O_4S_4$: C, 49.68; H, 4.26; N, 7.00; S, 16.77; found: C, 49.45; H, 4.15; N, 7.21; S, 16.50 %.

Mass spectrometry 778 (CdL^+, 100 %). **^{1}H NMR** ($CDCl_3$, ppm): 8.2 (s, 2H, N=CH), 7.3−6.8 (m, 16H, aromatics), 3.6 (t, 4H, N-CH_2), 3.2 (t, 4H, S-CH_2), 2.4 (s, 6H, CH_3). **IR** spectroscopy (KBr, cm^{-1}): ν (C=N) 1625 (s), ν(C−N) 1285 (s), $\nu_{as}(SO_2)$ 1249 (s), $\nu_s(SO_2)$ 1158 (s)

Physical measurements

Microanalyses were carried on a Fisons Instruments EA 1108 CHNS-O instrument. Infrared spectra were recorded, as KBr pellets on a Mattson Galaxy FT-i.r.2020 spectrophotometer in the 400−4000 cm^{-1} range, NMR spectra in $CDCl_3$ on a Bruker 300 AC spectrometer and ES mass spectra on a LC/MSD HP1100 spectrometer using CH_2Cl_2 as solvent.

Crystal structure determination

X-ray data were collected on a Bruker SMART 1000 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 293 K for all structures. The ω scan technique was employed to measure intensities for all crystals. Decomposition of the crystals did not occur during data collection. Corrections were applied for Lorentz and polarization effects and for absorption.

The structures were solved by direct methods, missing atoms were located in the difference Fourier maps and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2, using anisotropic displacement parameters for all non-hydrogen atoms. In all cases, hydrogen atoms were included using a riding model with C−H distances of 0.93−0.97 Å and fixed isotropic thermal parameters. A weighting scheme of the form $\omega = 1/\sigma^2(F)$ was introduced and the refinement proceeded smoothly to convergence.

Crystallographic programs used for the structure solutions and refinement were those included in SHELX97 [37]. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography. The crystal data and summary of data collection and structure refinement for these compounds are given in Table 1, and ORTEP 3 drawings [39], along with the numbering scheme used, are shown in Figures 1 and 2.

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers 643881 and 643882. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

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