Journal of Molecular Structure 985 (2011) 167–172

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Crystal structure, spectroscopic and redox behaviour of novel imidazolidine ligand

Cumali Çelik [a,b,*], Vickie McKee [c], Muhammet Köse [c], Mehmet Aslantaş [d], Mehmet Tümer [a]

[a] K.Maras Sütcü Imam University, Chemistry Department, 46100 K.Maras, Turkey
[b] Yalova University, Yalova Vocational College, 77100 Yalova, Turkey
[c] Univ. Loughborough, Dept. Chem., Loughborough, LE11 3TU Leics, England
[d] K.Maras Sütcü Imam University, Physics Department, 46100 K.Maras, Turkey

ARTICLE INFO

Article history:
Received 17 August 2010
Received in revised form 22 October 2010
Accepted 25 October 2010
Available online 3 November 2010

Keywords:
Schiff base
Electrochemical
Irreversible
Crystal structure
Imidazolidine

ABSTRACT

In this study, the Schiff base ligand 2,2′-[2-(3,4-dichlorophenyl)imidazolidine-1,3-diyl]bis{N-[(1E)-3,4-dichlorophenyl]ethanamine} (L) was prepared and characterized by the analytical and spectroscopic methods. The $^{1}H(^{13}C)$ NMR spectra of the ligand was recorded in DMSO-d6 solvent and obtained data confirm the proposed structure. Electrochemical properties of the ligand were investigated in the DMF solvent in the range 100–250 mV s^{-1} scan rates. The ligand showed both reversible and irreversible processes at these scan rates. The single crystal of the ligand (L) was obtained from MeOH solution, and its crystal structure analysis was performed by X-ray diffraction.

1. Introduction

Schiff bases are used as substrates in the preparation of a number of industrial and biologically active compounds via ring closure, cycloaddition and replacement reactions [1]. Moreover, Schiff bases derived from various heterocycles have been reported to possess cytotoxic [2], anticonvulsant [3], antiproliferative [4], antimicrobial [5], anticancer [6], and antifungal activities [7]. Mannich bases have gained importance due to their application in pharmaceutical chemistry. They have been encountered with antibacterial [8], anticancer [9], analgesic and anti-inflammatory [10], anticonvulsant [11], antimalarial [12], antiviral [13], and CNS depressant activities [14].

Imidazolidines are intermediates in the biosynthesis of nucleotides, and some of their metal complexes are found to be active as cytotoxic metallopharmaceuticals [15]. Several papers have been published on the preparation of symmetrical N,N′-disubstituted imidazolidines [16]; however, there are only a few reports on the preparation of unsymmetrical N,N′-disubstituted imidazolidines [17]. Most of the N,N′-disubstituted imidazolidines were prepared by the reaction of aldehydes with aliphatic 1,2-diamines (in which both amino groups are either primary or secondary) with cyanohalogens. Several of the imidazolidines are synthesized by the reaction of 1-substituted-2-nitramino-2-imidazolines with a mixture of nitric and sulfuric acids and the reaction of hydrobromides of mandelimic acid esters with alkylenediamine.

The design and synthesis of a new dinuclear complex requires good agreement between the stereochemical requirements of the metal and the special features of the ligand such as geometry of the available donor groups and spacers between the coordination groups [18]. Among various products from the condensation of aromatic aldehydes with α,ω-tetraamine containing both primary and secondary amino groups is a binucleating Schiff base with an in-built spacer imidazolidine ring, which can take up two same or different metal ions [19].

In this study, we prepared the compound 2,2′-[2-(3,4-dichlorophenyl)imidazolidine-1,3-diyl]bis{N-[(1E)-3,4-dichlorophenyl]ethanamine} (L) and characterized by the spectroscopic and analytical methods. Electrochemical properties of the ligand were investigated in the DMF solvent at the 100–250 mV s^{-1} scan rates. Molecular structure analysis was performed for ligand (L) by X-ray diffraction.

2. Experimental

2.1. General methods

3,4-Dichlorobenzaldehyde, triethylenetetraamine, NBu_4BF_4 and organic solvents were obtained from Fluka and used as received, unless noted otherwise. Elemental analyses (C, H, N) were performed using a LECO CHNS 932 elemental analyzer. IR spectrum was obtained using KBr discs (4000–400 cm^{-1}) on a Shimadzu

* Corresponding author at: K.Maras Sütcü Imam University, Chemistry Department, 46100 K.Maras, Turkey. Tel.: +90 344 2191495; fax: +90 344 2191042.
E-mail address: ccelik@ksu.edu.tr (C. Çelik).

0022-2860/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2010.10.037

8300 FT-IR spectrophotometer. The electronic spectra in the 200–500 nm range were obtained on a Perkin Elmer Lambda 45 spectrophotometer. Molar conductance measurement of the Schiff base ligand (L) was determined in methanol ($\sim 10^{-3}$ M) at room temperature using a Jenway Model 4070 conductivity meter. Mass spectrum of the ligand was recorded on an LC/MS APCI AGILENT 1100 MSD spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 instrument. TMS was used as internal standard and d_6-DMSO solvent.

Cyclic voltammograms were recorded on a Iviumstat Electrochemical workstation equipped with a low current module (BAS PA-1) recorder. The electrochemical cell was equipped with a BAS glassy carbon working electrode (area 4.6 mm^2), a platinum coil auxiliary electrode and a Ag^+/AgCl reference electrode filled with NBu_4BF_4 (0.1 M) in DMF solvent and adjusted to 0.00 V vs SCE. Cyclic voltammetric measurements were made at room temperature in an undivided cell (BAS model C-3 cell stand) with a platinum counter electrode and an Ag^+/AgCl reference electrode (BAS). All potentials are reported with respect to Ag^+/AgCl. The solutions were deoxygenated by passing dry nitrogen through the solution for 30 min prior to the experiments, and during the experiments the flow was maintained over the solution. Digital simulations were performed using DigiSim 3.0 for windows (BAS, Inc.). Experimental cyclic voltammograms used for the fitting process had the background subtracted and were corrected electronically for ohmic drop.

2.2. Preparation of the ligand (L)

A solution of triethylenetetramine (0.146 g, 1.00 mmol) in methanol (15 ml) was added drop wise to an ice cold methanolic solution (30 ml) of 3,4-dichlorobenzaldehyde (0.525 g, 3.00 mmol) with stirring the yellow solution was stirred for 1 h and the solvent was evaporated in air. The yellow solid was separated by filtration through G4 sintered bed and washed thoroughly with hexane and water. Finally, the isolated compound was dried *in vacuo* over P_4O_{10}. Single crystals of the ligand (L) were obtained by recrystallization from CH_3OH solution.

L: Yield: 80%, color: light yellow, m.p. 81–83 °C. Analysis Calc. for $C_{27}H_{24}Cl_6N_4$: C, 52.54; H, 3.92; N, 9.08%. Found: C, 52.56; H, 3.95; N, 9.10%. Mass spectrum (LC/MS APCI): m/z 617 (M^+=L^+). Infrared spectrum (cm^{-1}, KBr disc): 2960, 2845 ν (CH_2), 1625 ν (CH=N). UV–Vis: (λ_{max}, nm; ε_{max}, M^{-1} cm^{-1}), CH_3OH as solvent): 342 (1805), 315 (1900), 286 (1.6×10^{-3}), 250 (7.2×10^{-3}). ^{1}H NMR: (DMSO-d6 as solvent, δ in ppm): 2.4 (4H, *m*, H8 and H13), 2.7 (4H, *m*, H9 and H12), 3.44 (4H, *m*, H10 and H11), 3.75 (H, *m*, H21), 7.23–7.29 (4H, *m*, H1, H2, H19 and H20), 7.34–7.36 (2H, *m*, H5 and H16), 7.66–7.67 (3H, *m*, H23, H26 and H27), 8.25 (2H, *s*, H7 and H14). ^{13}C NMR (DMSO-d6 as solvent, δ in ppm): 51.80 (C8 and C13), 53.35 (C9 and C12), 60.61 (C10 and C11), 89.60 (C21), 96.14 (C6 and C15), 104.15 (C22), 110.70 (C5 and C16), 11.20 (C1 and C20), 117.40 (C2 and C19), 119.40 (C23), 126.35 (C26 and C27), 143.10–144.81 (C3, C4, C17, C18, C24 and C25), 163.50 (C7 and C14). Λ (1×10^{-3} M): 1.5 Ω^{-1} cm^2 mol^{-1}.

2.3. X-ray structure solution and refinement for the Schiff base ligand (L)

A block colorless crystal with dimensions $0.34 \times 0.25 \times 0.16$ mm was chosen for the structure determination. Diffraction experiment was carried out at 150(2) K on a Bruker APEX-II CCD diffractometer. The structure was solved by SHELXS-97 [20] and refined by SHELXL-97 [21] software package. The H atom on C7 and C14 were located in difference maps and their coordinates and U_{iso} values were refined freely. In the final stage of refinement, the other H atoms were located in geometrically idealized positions [0.93–0.98 (CH) and 0.97 Å (CH_2)] and treated as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(C7 and C14). The final cycle of the refinement included 342 variable parameters $R_1 = 0.0595$, $\omega R_2 = 0.1013$ where $\omega = 1/[\sigma^2 (F_o^2) + (0.044\ P)^2 + 1.1428\ P]$ where $P = (F_o^2 + 2F_c^2)/3$ were obtained. A summary of the key crystallographic information is given in Table 1.

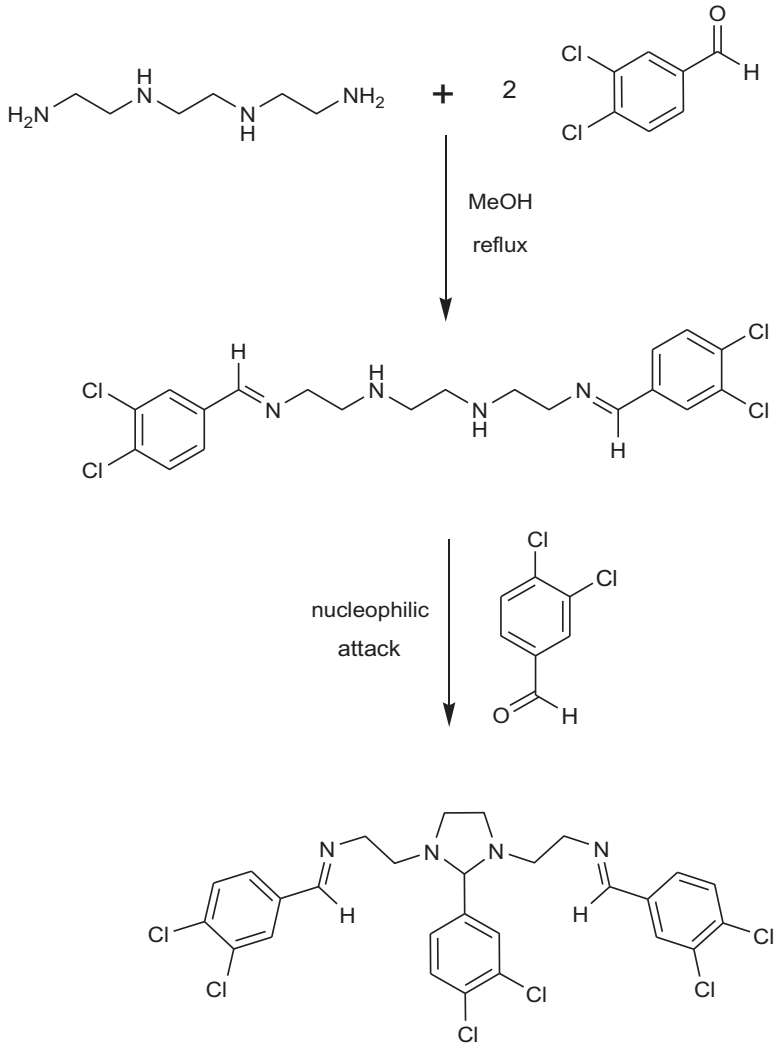
3. Results and discussion

The reaction of triethylenetetramine and 3,4-dichlorobenzaldehyde in 1:3 M ratio in methanol affords the μ-bis(tetradentate) ligand (L) through the formation of an imidazolidine ring in place of the ethylenediamine part of the parent tetradentate precursor. This semi-rigid 3,4-dichlorophenyl-substituted five-membered imidazolidine ring inside the ligand backbone acts as a spacer-cum-bridging-cum-heterocyclic backbone unit. Synthesis of the compound (L) had been achieved in a two step reaction which was initiated by an inter-molecular nucleophilic attack on the incoming 3,4-dichlorobenzaldehyde carbon atom by imine nitrogen of the parent tetradentate ligand as shown in Scheme 1. In the second step of the reaction, the intra-molecular rearrangement (*via* SN^2 attack) takes place which finally introduces the imidazolidine ring through an alkylating cyclization process centred on the two secondary amine functions of the intermediate species. A plausible mechanism for this reaction leading to the final ligand (L) is given in Scheme 1. The analytical, spectroscopic and physical data of the Schiff base ligand (L) are given in the experimental section. The analytical data confirm that the 3,4-dichlorobenzaldehyde to triethylenetetraamine ratio is 3:1. The ligand (L) is soluble in common polar organic solvents such as EtOH, MeOH, $CHCl_3$, and CH_2Cl_2. The ligand (L) is a very stable solid at room temperature without decomposition. The ligand (L) was obtained as light yellow crystals with 80% yield. This yield was a normal value for the Schiff base ligand. The low molar conductance value (experimental section) of 1×10^{-3} M solution in methanol showed to be non-electrolytes [22]. From the methanol solution, we obtained suitable single crystals for X-ray diffraction analysis.

The ^{1}H- and ^{13}C NMR spectra of the ligand (L) were recorded using DMSO-d6 as a solvent, and the spectral data are given in

Table 1
Crystal data and structure refinement for the title compound.

Empirical formula	$C_{27}H_{24}Cl_6N_4$
Formula weight	617.20
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P $2_1/c$
Cell dimensions	a = 6.056(10) Å
	b = 20.546(3) Å
	c = 22.270(4) Å
	β = 91.179(3)°
Cell volume	2771(5) Å^3
Z	4
Density (calculated)	1.480 mg/m^3
Absorption coefficient	0.646 mm^{-1}
F_{000}	1264
Crystal size	$0.34 \times 0.25 \times 0.16$ mm
θ(°) range for data collection	1.35–28.37
Index ranges	$-8 \leqslant h \leqslant 8$
	$-27 \leqslant k \leqslant 27$
	$-29 \leqslant l \leqslant 29$
Reflections collected/unique	27657/6897 [R(int) = 0.0458]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6897/0/342
Goodness-of-fit on F^2	1.025
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0413, wR_2 = 0.0935
Largest diff. peak and hole	0.318 and −0.263 eÅ^{-3}
CCDC deposition number	740397



Scheme 1. Probable mechanism for the formation of the Schiff base ligand.

experimental section. The ligand has an symmetric nature. The outher benzene rings are equivalent but inner benzene ring is not. Therefore, aromatic ring protons and carbon atoms were seen in different regions. As seen also from the structure of the ligand (L), the molecule have two azomethine groups, three benzene rings, three ethylene (—CH_2—CH_2—) and one methine (—CH—) groups. In the ^{1}H NMR spectrum, the hydrogen atoms of the azomethine groups were seen as a singlet at the δ 8.25 ppm. The aromatic rings protons (9H) were seen in the range δ 7.23–7.67 ppm range as a multiplet. Ethylene hydrogen atoms are in three different environments. One of them (—CH_2—CH_2—) were seen in the δ 2.40–2.70 ppm ranges. Others (—CH_2—CH_2—) were in the δ 3.44–3.75 ppm ranges, as a multiplet. The multiplet at 3.75 ppm can be attributed to the proton of the methine group.

In order to get further information about the ligand (L), the ^{13}C NMR spectrum was investigated. The azomethine carbon atoms (C7 and C14) have similar environments. In the ligand, the signal of the azomethine (—CH=N—) carbon atoms was shown at δ 163.50 ppm. The aromatic ring C atoms were shown in the δ 144.81–96.14 ppm range. The ligand has an imidazolidine ring. The signal of the (C21) numbered carbon atom of the imidazolidine ring was shown at the δ 89.60 ppm. In the ^{13}C NMR spectrum of the ligand, the methylenic carbon atoms of the =N—CH_2— groups were seen at the 60.61. The carbon atoms of the —CH_2—CH_2— groups were seen in the δ 51.80–53.35 ppm range.

The mass spectral studies for the ligand were done and obtained data are given in the experimental section. The mass spectrum of the ligand (L) shows molecular ion peak ($[M]^+$, 100%) at m/z 617. Moreover, the fragmentation peak at m/z 618 (35%) can be attributed to the $[M+1]^+$.

The infrared spectral data of the ligand (L) were given in the experimental section. In the spectrum of the ligand, the ν (CH_2) of the butane linkage were shown at the 2960 and 2845 cm^{-1}. The ν (CH=N) of the azomethine group was shown at the 1625 cm^{-1}.

Electronic spectrum of the prepared Schiff base ligand (L) in CH_3OH displays main features in the different regions. These wavelengths are at 250, 286, 315 and 342 nm. The intense absorption bands at short wavelengths 250 and 286 nm may be assigned for π—π^* aromatic rings transitions. The weak broad absorption bands at the 315 and 342 nm may be assigned to the n—π^* and π—π^* electronic transition associated with the C=N linkages.

The ORTEP [23,24] diagram of the molecule indicating atom numbering Scheme 1 with thermal ellipsoids at 50% probability is illustrated in Fig. 1. The crystal packing in the unit cell is shown in Fig. 2. Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Selected bond lengths, bond angles and torsion angles are listed in Table 3. The PARST [25] and PLATON [26] programs were used for geometrical calculation of the molecule compound.

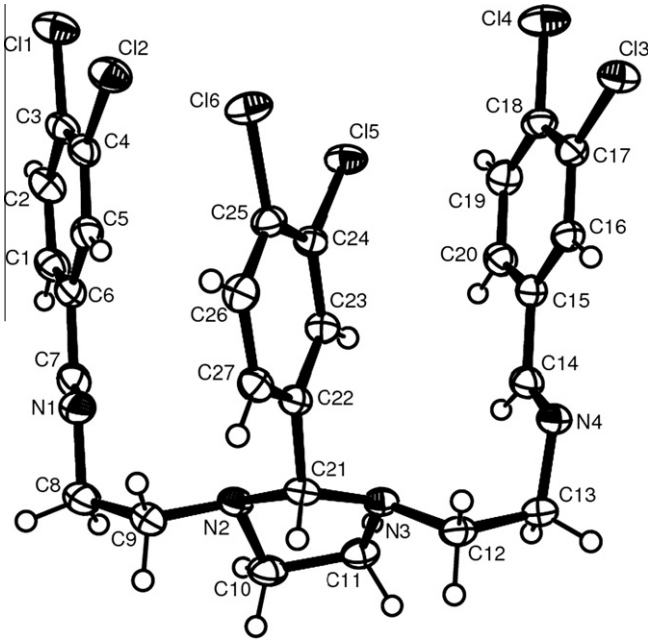


Fig. 1. Molecular structure of the title compound with atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

We present the crystal structure of the ligand, ($C_{27}H_{24}Cl_6N_4$), which contains two [(3,4-dichlorophenyl)methylidene]ethamine, a dichlorophenyl groups, and a five-membered imidazolidine ring system. Individually each dichlorophenyl groups in the molecule is almost planar with showing small distortions. The C9, C12, and C26 atoms deviate from the each dichlorophenyl best plane by only −0.375(2), 1.086(2), and −0.046(2) Å, respectively, so lie nearly in their planes. In the five-membered imidazolidine ring system, N2 atom projects out of plane and the ring system exhibits in a distorted half-chair conformation.

The bond lengths and angles are generally within normal ranges in the compound moiety. All bond lengths and angles in the C1—C6, C15—C20 and C22—C27 benzene rings have normal Csp^2—Csp^2 values and are in the expected ranges; the average C—C bond lengths within these rings are 1.388(4), 1.386(3) and 1.392(3) Å, respectively. The *A*/*B*, *A*/*C* and *B*/*C* dihedral angles between the planes of [(3,4-dichlorophenyl)methylidene]ethamine groups and, a dichlorophenyl group, respectively, *A*(C1—C6, Cl1, Cl2), *B*(C15—C20, Cl3, Cl4) and *C*(C22—C27, Cl5, Cl6) are 10.02(2)°, 48.12(4)° and 46.22(4)° which imply that dichlorophenyl group (C) rotate oppositely from the planarity of the molecule (Fig. 2).

As a result of X-ray diffraction study demonstrated that weak C—H···N type intra-molecular, and C—H···N and C—H···Cl types inter-molecular hydrogen-bonding interactions are observed in the molecular structure.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^3 \times 10^3$). *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)
Cl(6)	4337(1)	6448(1)	2414(1)	33(1)
Cl(3)	282(1)	5862(1)	4803(1)	34(1)
Cl(4)	−4300(1)	5396(1)	4255(1)	44(1)
Cl(2)	−735(1)	6253(1)	1265(1)	37(1)
Cl(5)	−313(1)	6696(1)	2995(1)	31(1)
Cl(1)	−5220(1)	5864(1)	618(1)	41(1)
N(3)	−26(3)	9225(1)	3519(1)	23(1)
N(2)	−206(3)	9366(1)	2498(1)	25(1)
C(16)	−1194(3)	7081(1)	4595(1)	25(1)
N(4)	−466(3)	8459(1)	4643(1)	28(1)
C(17)	−1660(3)	6424(1)	4555(1)	26(1)
C(21)	1336(3)	9178(1)	2985(1)	23(1)
C(1)	−5722(4)	7795(1)	766(1)	33(1)
C(25)	3526(3)	7227(1)	2607(1)	24(1)
C(23)	798(3)	7968(1)	2988(1)	23(1)
C(27)	4285(3)	8375(1)	2661(1)	25(1)
C(18)	−3678(4)	6218(1)	4307(1)	29(1)
C(4)	−2632(3)	6842(1)	1052(1)	28(1)
C(24)	1457(3)	7339(1)	2851(1)	23(1)
C(15)	−2736(3)	7538(1)	4389(1)	26(1)
C(26)	4950(3)	7744(1)	2517(1)	26(1)
C(6)	−3694(4)	7971(1)	1018(1)	29(1)
C(7)	−3123(4)	8659(1)	1143(1)	32(1)
C(2)	−6191(4)	7148(1)	636(1)	33(1)
C(13)	−170(4)	9163(1)	4618(1)	29(1)
C(19)	−5211(4)	6669(1)	4098(1)	32(1)
C(14)	−2257(4)	8239(1)	4430(1)	27(1)
C(3)	−4647(4)	6672(1)	782(1)	30(1)
C(20)	−4740(4)	7324(1)	4140(1)	30(1)
N(1)	−1170(3)	8819(1)	1277(1)	34(1)
C(22)	2196(3)	8493(1)	2885(1)	22(1)
C(9)	902(4)	9535(1)	1942(1)	32(1)
C(12)	1215(3)	9335(1)	4075(1)	26(1)
C(5)	−2151(4)	7486(1)	1163(1)	28(1)
C(11)	−1794(4)	9700(1)	3394(1)	29(1)
C(8)	−668(4)	9497(1)	1404(1)	36(1)
C(10)	−1458(4)	9908(1)	2750(1)	32(1)

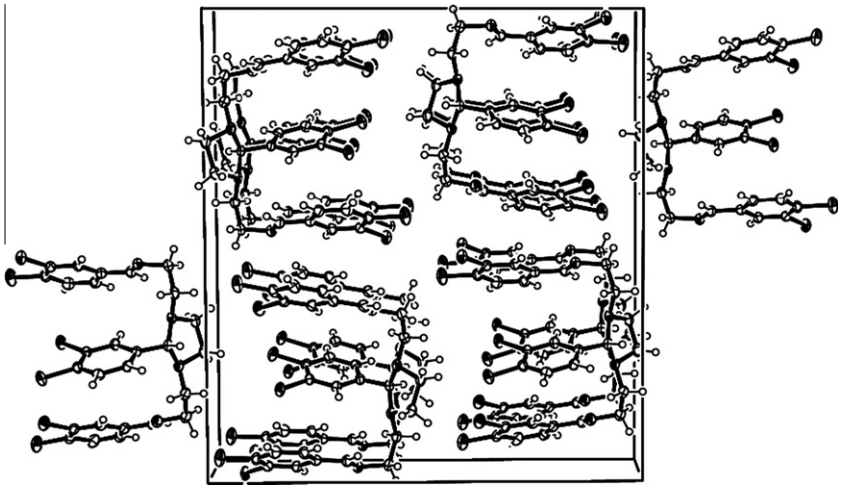


Fig. 2. The crystal packing of the title compound along (1 0 0) direction.

Table 3
Selected bond lengths (Å), bond angles (°) and torsion angels (°).

CL6—C25	1.731(2)	Cl3—C17	1.731(2)
Cl4—C18	1.734(2)	Cl2—C4	1.728(2)
Cl5—C24	1.734(2)	Cl1—C3	1.733(2)
N3—C12	1.453(3)	N3—C21	1.464(3)
N3—C11	1.471(3)	N2—C9	1.463(3)
N2—C10	1.465(3)	N2—C21	1.468(3)
N4—C14	1.259(3)	N4—C13	1.459(3)
C7—N1	1.257(4)	N1—C8	1.453(3)
C7—N1—C8	119.3(2)	C14—N4—C13	116.60(19)
N1—C8—C9	109.15(18)	N4—C13—C12	109.25(16)
N2—C10—C11	103.22(16)	N3—C11—C10	104.74(17)
N3—C21—N2	102.83(18)	N3—C21—C22	112.44(15)
C27—C22—C23	118.97(19)	C9)—N2—C21	113.09(19)
C12—N3—C21	114.35(18)	C21—N3—C11	108.11(16)
C9—N2—C21—N3	163.68(16)	C12—N3—C21—N2	−155.38(15)
C11—N3—C21—N2	−26.09(19)	C10—N2—C21—N3	40.45(18)
N2—C9—C8—N1	−71.4(2)	N4—C13—C12—N3	70.2(2)
C13—N4—C14—C15	175.99(18)	C6—C7—N1—C8	−179.29(19)
C5—C6—C7—N1	12.4(3)	C20—C15—C14—N4	−179.0(2)
C21—N2—C10—C11	−39.0(2)	N3—C11—C10—N2	22.4(2)

Cyclic voltammetric studies of the ligand (L) were run in two different concentrations (1×10^{-3} and 1×10^{-4} M DMF solutions) at 293 K using 0.1 M NBu_4BF_4 as supporting electrolyte. Unless otherwise stated, all potentials quoted refer to measurements run at a scan rates ('v') of 100, 150, 200 and 250 mV s^{-1} and against an Ag^+/AgCl reference electrode. All voltammetric measurements were performed using a glassy carbon disc electrode as a working electrode. The results of these experiments were summarized in Table 4. The electrochemical curves of the ligand (L) at 100, 150 and 200 mV s^{-1} scan rates are shown in Fig. 3. In order to study the effect of the concentration of the ligand, electrochemical properties were investigated using two different concentrations of the ligand. These concentrations are 1×10^{-3} and 1×10^{-4} M. As shown also from Fig. 3 and Table 4, at the all scan rates, the ligand (L) has two cathodic and anodic peak potentials. In the 1×10^{-3} M solution, in the 100–250 mV s^{-1} range, the values in the −1.19–0.7 V and −1.27–0.39 V ranges can be attributed to the anodic and cathodic peak potentials, respectively. At the 100 and 150 mV s^{-1} scan rates, all redox processes are irreversible. In other words, at the 200 and 250 mV s^{-1}, the ligand shows the reversible redox couples at −0.60 V (E_{pa}) and −0.51 V (E_{pc}) with −0.60 V (E_{pa}) and −0.56 V (E_{pc}) potentials [27]. This situation is shown in Fig. 4. In the −1.19–0.07 V range, the ligand shows the irreversible processes. In the 1×10^{-4} M concentration of the ligand, in the 100–250 mV s^{-1} range, the ligand shows the peak potentials in the −1.50–0.55 V (E_{pa}) and −1.55–0.55 V (E_{pc}) ranges, respectively. The ligand has the reversible processes at −0.66 V (E_{pa})/0.55 V (E_{pc}), 0.55 V (E_{pa})/−0.66 V (E_{pc}), 0.50 V (E_{pa})/−0.54 V (E_{pc}) and 0.49 V (E_{pa})/−0.54 V (E_{pc}) (Fig. 4). As the scan rate increases, the cathodic and anodic peak potentials were shifted to the positive regions. In the lower concentration, while the anodic peak potentials shift to the positive region, the cathodic potentials were shifted to the positive region at the 100 mV s^{-1} scan rate. In the reducing process, the azomethine (—CH=N—) groups convert to the secondary amine (—CH_2—NH—) derivatives [28]. As the chloride (—Cl) substituted groups on the benzene rings give electrons to the aromatic rings by the mesomeric effect, the peak potentials shift to the negative regions.

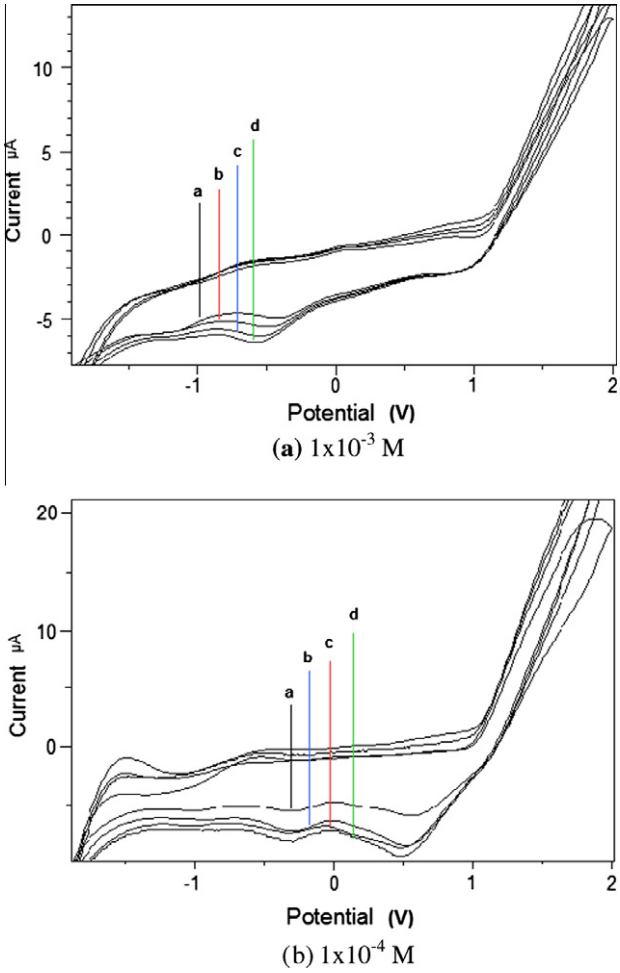


Fig. 3. Cyclic voltammograms of the ligand (L) in the presence of 0.1 M NBu_4BF_4 in DMF (sr: (a) 100, (b) 150, (c) 200 and (d) 250 mV s^{-1}). (a) 1×10^{-3} M and (b) 1×10^{-4} M.

4. Conclusion

In summary, we have successfully synthesized a tetradentate Schiff base ligand (L) from the reaction of the aliphatic tetraamine and 3,4-dichlorobenzaldehyde in methanol solution. During the synthesis of the ligand (L), an imidazolidine derivative has been obtained. This semi-rigid 3,4-dichlorophenyl-substituted five-membered imidazolidine ring inside the ligand backbone acts as

Table 4
Electrochemical data of the title compound (L).[a]

Scan rates (mV s^{-1})	Conc.	E_{pa} (V)	E_{pc} (V)	$^iE_{1/2}$ (mV)	$^i\Delta E_p$ (mV)	Scan rates (mV s^{-1})	Conc.	E_{pa} (V)	E_{pc} (V)	$^iE_{1/2}$ (mV)	$^i\Delta E_p$ (mV)
100	1×10^{-3} M	−0.54, −0.07	−1.27, 0.39	–	730, −320	100	1×10^{-4} M	−1.50, −0.66	−0.27, 0.55	605	−1430, 50
150	1×10^{-3} M	−0.47, −1.19	−0.62, 0.03	–	150, 1187	150	1×10^{-4} M	−0.27, 0.55	−1.50, −0.66	605	1430, −110
200	1×10^{-3} M	−0.60, 0.07	−1.19, −0.51	−45	590, −470	200	1×10^{-4} M	−0.30, 0.50	−1.50, −0.54	52	1200, −40
250	1×10^{-3} M	−0.60, 0.05	−1.17, −0.56	−20	570, −510	250	1×10^{-4} M	−0.30, 0.49	−1.55, −0.54	515	1250, −50

[a] Supporting electrolyte: tetrabutylammonium tetrafluoroborat (Bu_4NBF_4) (0.1 M); concentration of the compound: 1×10^{-3} and 1×10^{-4} M. All the potentials are referenced to Ag/Ag^+ (0.03 M $AgNO_3$); where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively. $E_{1/2} = 0.5 \times (E_{pa} + E_{pc})$, $\Delta E_p = E_{pa} - E_{pc}$.

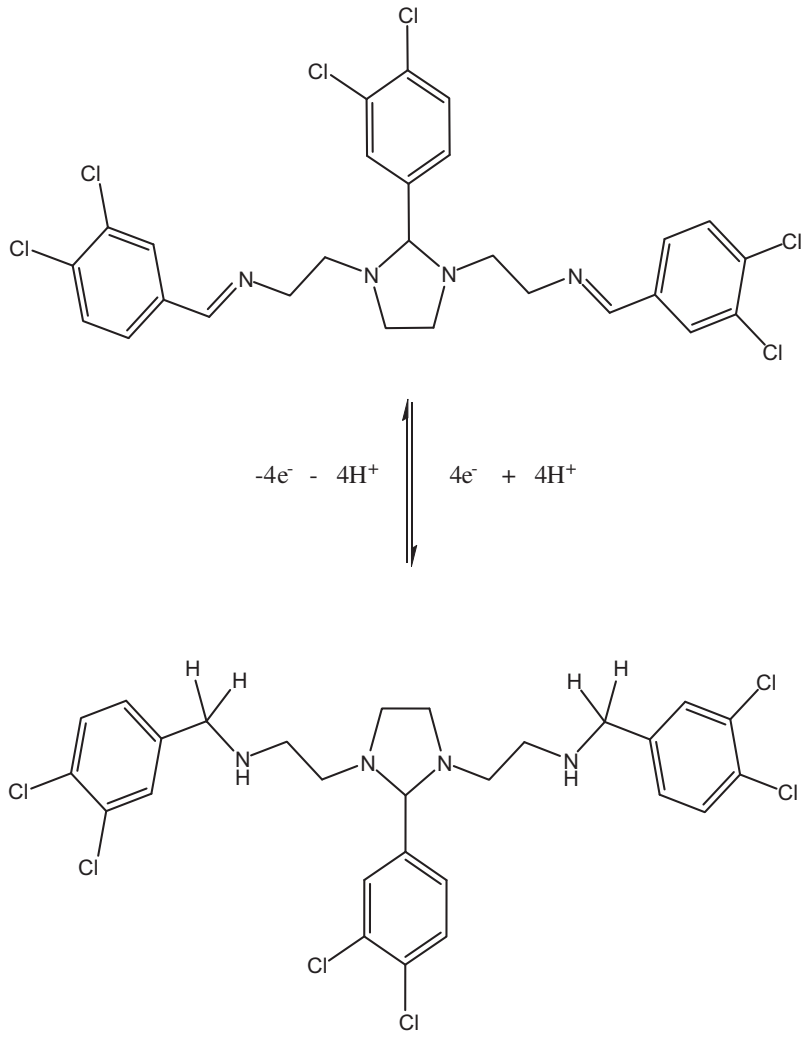


Fig. 4. Reduction–oxidation processes of the ligand in DMF solution.

a spacer-cum-bridging-cum-heterocyclic backbone unit. In the electrochemical studies of the ligand, the reversible and irreversible redox processes were shown. In the X-ray diffraction analysis of the ligand, weak intra-(C—H···N), and inter-molecular (C—H···N and C—H···Cl) hydrogen-bonding interactions were observed in the molecular structure.

5. Supplementary data

Full crystallographic data for the reported ligand (L) has been deposited with the Cambridge Crystallographic Data Center, CCDC 740397. Copies of this information may be obtained by writing your request to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] D. Karia, P.H. Parsania, Asian J. Chem. 11 (1999) 991–995.
[2] M.T. Tarafder, A. Kasbollah, N. Saravan, K.A. Crouse, A.M. Ali, O.K. Tin, J. Biochem. Mol. Biol. Biophs. 6 (2002) 85–91.
[3] İ. Küçükgüzel, Ş.G. Küçükgüzel, S. Rollas, G. Ötük-Sanış, O. Özdemir, İ. Bayrak, T. Altuğ, Farmaco 59 (2004) 893–901.
[4] P. Vicini, A. Geronikaki, M. Incerti, B. Busonera, G. Poni, C.A. Kabras, P.L. Colla, Bioorg. Med. Chem. 11 (2003) 4785–4789.
[5] B. Kahveci, O. Bekircan, S.A. Karaoğlu, Indian J. Chem. 44B (2005) 2614–2617.
[6] O. Bekircan, B. Kahveci, M. Kucuk, Tur. J. Chem. 30 (2006) 29–40.
[7] W.M. Singh, B.C. Dash, Pesticides 22 (1988) 33–37.
[8] B.S. Holla, M.K. Shivananda, M.S. Shenoy, G. Antony, Farmaco 53 (1998) 531–535.
[9] B.S. Holla, B. Veerendra, M.K. Shivananda, B. Poojary, Eur. J. Med. Chem. 38 (2003) 759–767.
[10] E. Gökçe, G. Bakir, M.F. Şahin, E. Küpeli, E. Yeşilada, Arzneim. Forsch. 55 (2005) 318–325.
[11] J.R. Dimmock, S.S. Jonnalagadda, O.A. Phillips, E. Erciyas, K. Shyam, H.A. Semple, J. Pharm. Sci. 81 (1992) 436–440.
[12] F. Lopes, R. Capela, J.O. Goncaves, P.N. Horton, M.B. Hursthouse, J. Iley, C.M. Casimiro, J. Bom, R. Moreire, Tetrahedron Lett. 45 (2004) 7663–7666.
[13] D. Sriram, T.R. Bal, P. Yogeesswari, Med. Chem. Res. 14 (2005) 211–228.
[14] J. Knabe, H.P. Buch, W. Schmitt, Arch. Pharm. Chem. Life Sci. 316 (1983) 1051–1053.
[15] V. Sharma, C.L. Crankshaw, D. Piwnica-Worms, J. Med. Chem. 39 (1996) 3483–3490.
[16] H. Heaney, G. Papageorgiou, R.F. Wilkins, Tetrahedron 53 (1997) 14381–14396.
[17] M. Boca, P. Baran, R. Bock, H. Fuess, G. Kickelbick, W. Linert, F. Renz, I. Svoboda, Inorg. Chem. 39 (2000) 3205–3212.
[18] E.C. Constable, Angew. Chem. Int. Ed. Engl. 30 (1991) 1450–1451.
[19] Y. Maeda, H. Oshio, Y. Tanigawa, T. Onoki, Y. Takashima, Bull. Chem. Soc. Jpn. 64 (1991) 1522–1527.
[20] G.M. Sheldrick, (SHELXS-97), University of Gottingen, Germany, 1997.
[21] G.M. Sheldrick, (SHELXL-97), University of Gottingen, Germany, 1997.
[22] H. Demirelli, M. Tümer, A. Gölcü, Bull. Chem. Soc. Jpn. 79 (2006) 867–875.
[23] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565–566.
[24] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.
[25] M. Nardelli, J. Appl. Crystallogr. 28 (1995) 659.
[26] A.L. Spek, PLATON, University of Utrecht, The Netherlands, 2003.
[27] M. Dolaz, V. McKee, A. Gölcü, M. Tümer, Curr. Org. Chem. 14 (2010) 281–288.
[28] M. Dolaz, V. McKee, A. Gölcü, M. Tümer, Spectrochim. Acta Part A 71 (2009) 1648–1654.