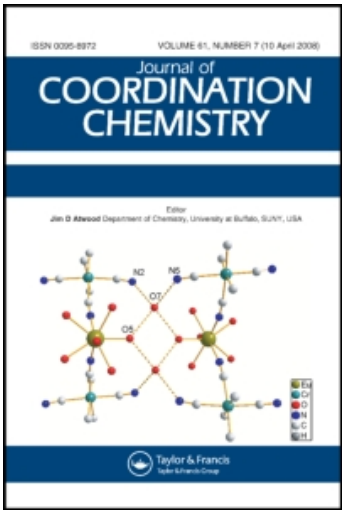

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Characterization and Electronic Properties of a Symmetric Bidentate Schiff-Base Ligand and Its Complex with CadmIum(II)

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Online publication date: 15 September 2010

To cite this Article Sheikhshoaei, Iran(2003) 'Synthesis, Characterization and Electronic Properties of a Symmetric Bidentate Schiff-Base Ligand and Its Complex with CadmIum(II)', Journal of Coordination Chemistry, 56: 6, 463 — 466
To link to this Article: DOI: 10.1080/0095897031000099974
URL: http://dx.doi.org/10.1080/0095897031000099974

J. Coord. Chem., 2003, Vol. 56, No. 6, pp. 463–466

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SYNTHESIS, CHARACTERIZATION AND ELECTRONIC PROPERTIES OF A SYMMETRIC BIDENTATE SCHIFF-BASE LIGAND AND ITS COMPLEX WITH CADMIUM(II)

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(Received 22 May 2002; Revised 16 July 2002; In final form 05 January 2003)

A symmetric bidentate Schiff-base ligand and its complex with Cd(II) is described. The ligand and its complex were characterized by microanalysis, UV–Vis, GC-Mass and FT-IR spectroscopic methods. The present work also studied the structures and electronic properties of the bidentate Schiff-base ligand by using *ab initio* and AM1 molecular orbital methods. *Ab initio* and AM1 geometrical predictions have been compared.

The analysis of molecular orbitals (MOs) indicates that the N(3) and N(6) atoms could be the coordination sites in this ligand.

Keywords: Schiff base; Theoretical methods; Electronic properties

INTRODUCTION

There is considerable interest in the synthesis and characterization of Schiff-base complexes containing different central metal atoms complexes of Cu, Ni and Pd. These have been studied in great detail for their various crystallographic features, enzymatic reactions, steric effects and structure-redox relationships. The charge transfer mechanisms of Schiff-base ligands with coordination metal compounds have gained importance recently, in relation to the study of several biological and catalytic processes [1].

MO calculations are performed on the Schiff-base ligand by using AM1 Hamiltonian SCF-MO methods with the MOPAC 6.0 program [2,3] and using the *ab initio* method with the Hyperchem 5.01 program [4].

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0095897031000099974

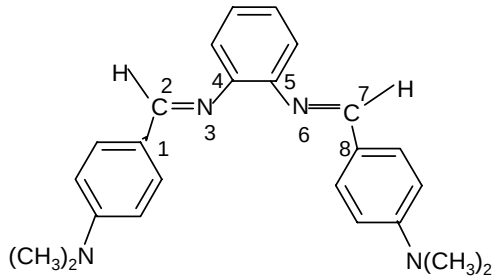

FIGURE 1 Structure of the ligand.

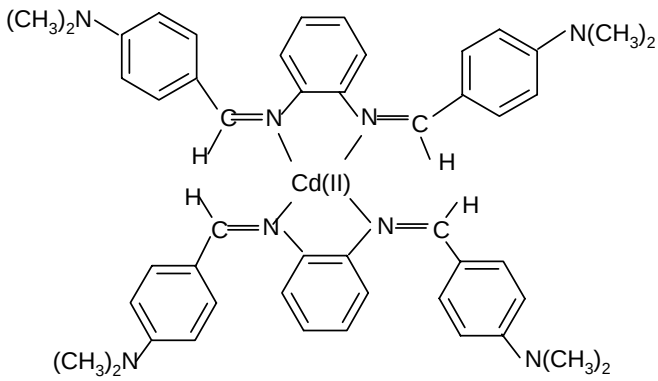

FIGURE 2 Structure of the metal complex.

RESULTS AND DISCUSSION

Preparation of the Schiff-base Ligand

For preparation of the Schiff-base (L) (Fig. 1), 1,2-phenylenediamine (1 mmol), was dissolved in absolute ethanol (15 mL), and was added with stirring to a solution of *p*-*N*,*N*-dimethyl benzaldehyde (2 mmol) in hot ethanol (15 mL). The mixture was stirred for 4 h, until the product precipitated. The mixture was filtered and washed sparingly with hot ethanol several times, yield (63%).

Preparation of the Cd(II) Complex

A hot solution of Cd $(NO_3)_2 \cdot 4H_2O$ (1 mmol) in ethanol was added to a hot solution of ligand (2 mmol) in ethanol within 35 min. The solution obtained was stirred and refluxed for 3 h, then was filtered and washed several times with hot ethanol and dried in vacuo at 80°C, yield 45%. The physical data and analytical results of the ligand and its Cd(II) complex (Fig. 2) are listed in Table I.

INFRARED SPECTRA

The IR spectral data for ligand (L) and its Cd(II) complex (CdL_2) are given in Table II.

The stretching mode of C=N in the CdL_2 complex shifted to lower frequency by 20 cm^{-1} in comparison to the free ligand.

TABLE I Elemental analysis data and some physical properties of the Schiff-base ligand and its Cd(II) complex

Compound (formula)	*Color*	*Yield* (%)	*Found (calcd)* (%)			*Formula weight* ($g\,mol^{-1}$)	*Conductivity*[a] ($Ohm^{-1}\,cm^2\,mol^{-1}$)	*Melting point* (°C)
			C	H	N			
Ligand (L) $C_{24}H_{26}N_4$	Yellow	63	77.02 (77.83),	7.98 (7.02),	15.11 (15.13)	370	27	179
Complex $CdL_2(NO_3)_2$ $C_{48}H_{52}N_{10}O_6Cd$	White	45	57.98 (58.99),	5.01 (5.32),	13.99 (14.33)	976.4	32	205

[a]Concentration = 10^{-3} M in DMF at 25°C.

TABLE II IR and Far-IR spectral data of the ligand and its Cd(II) complex (cm^{-1})

Compound (formula)	$\upsilon_{C=N}$	$\upsilon_{Cd=N}$
Ligand (L) $C_{24}H_{26}N_4$	1645	–
Cd Complex $CdL_2(NO_3)_2$ Cd $C_{48}H_{52}N_{10}O_6$	1625	434

TABLE III Molecular orbitals of the bidentate Schiff-base ligand

MO	*Symmetry*	*E* (eV)	*Contribution of the AO in the MO*	
			N(3)	*N(6)*
Ψ_{65}	σ	−9.583	0.5500	0.0000
Ψ_{66}	σ	−9.575	0.0000	0.5437
Ψ_{67}	π	−9.542	0.0000	0.0000
Ψ_{68}	π	−9.387	0.0000	0.0000
Ψ_{69}	π	−8.886	0.0062	0.0000
Ψ_{70}	π	−8.021	0.0003	0.0001
Ψ_{71}	π	−7.716	0.0000	0.0000

Method of Calculation

AM1 eigenvalues and the contribution of the atomic orbitals (AO) to the frontier MOs of L are reported in Table III. The MOs are named $\Psi_1, \Psi_2, \ldots, \Psi_n$ according to energy order. The MO will be able to take part in δ-bonding with metal ion and the MOs more likely to combine with the metal orbital [5]. The symmetry of MOs are also shown in Table III. From this table, the MOs Ψ_{65} and Ψ_{66} are mainly located on N(3) and N(6) atoms. The contribution of N(3) and N(6) atomic orbitals are larger than the other atoms and the N(3) and N(6) atoms could be expected to be the coordination sites [6].

The bond lengths and angles of the Schiff-base ligand (L) and its Cd(II) complex are shown in Table IV. These calculations show that the Cd(II) complex has square planar or nearly square planar symmetry.

TABLE IV Comparison of selected bond lengths (Å) and bond angles (°) for the ligand and its Cd(II) complex calculated by AM1, 6-31G** and ZINDO/1 methods

	Ligand (AM1)	*Ligand (6-31G**)*	*Complex (ZINDO)*
C(1)–C(2)	1.462	1.432	1.478
C(2)–N(3)	1.292	1.221	1.227
N(3)–C(4)	1.402	1.398	1.432
C(4)–C(5)	1.441	1.401	1.440
C(1)–C(2)–N(3)	122.863	121.610	119.598
C(2)–N(3)–C(4)	122.802	121.350	118.938
C(1)–C(2)–N(3)–C(4)	180	179.983	177.236

EXPERIMENTAL

Solvent and Reagents

All chemicals used in this work were of reagent grade: 1,2-phenylenediamine; 4-*N*,*N*-dimethyl benzaldehyde and cadmum nitrate; tetrahydrate (reagent grade, Merck). Absolute ethanol was used in this work.

Measurements

The prepared Schiff-base ligand (L) and its Cd(II) complex (CdL_2) were characterized by microanalysis, UV–Vis and FT-IR spectroscopic methods. The Microanalytical Laboratory, Research Institute of Petroleum Industry of Iran determined the elemental analysis. FT-IR spectra were recorded on a Shimadzu DR-8001 spectrophotometer (KBr disks) in the range of 400–4000 cm^{-1}, and Far-IR spectra (500–1000 cm^{-1}) were recorded in Nujol mull between polyethylene sheets. The UV–Vis spectra were recorded with a Beckman DU-7000 spectrometer and mass spectra were recorded on a *Finnigenmat* GC-MSDS spectrometer model 8430.

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