IJARSCT

International Journal of Advanced Research in Science, Communication and Technology

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

ISSN: 2581-9429

Volume 3, Issue 1, May 2023

Impact Factor: 7.301

Synthesis, Structural and Spectroscopic Characterization of a Ni(II) Dimeric Complex with a Tridentate NNO donor Schiff Base Ligand: Coexistence of Square Planar and Octahedral Geometries

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Abstract: *A new Ni(II) complex, $[Ni_2L_2(OH)(OH_2)]ClO_4{\cdot}CH_2Cl_2$ (**1**), was synthesized using a tridentate N,N,O-donor Schiff base ligand, HL, derived from the condensation of salicylaldehyde and N,N-dimethylethane-1,2-diamine. The complex was characterized by X-ray structural analysis and spectroscopic studies. The crystal structure reveals a Ni(II) dimer in which the two Ni atoms adopt distinct coordination environments: one in a square planar geometry and the other in an octahedral geometry. These Ni atoms are bridged by a phenoxo oxygen atom from the ligand and a hydroxo group.*

Keywords: Tridentate Schiff base, Nickel(II), Crystal structure, Dinuclear complex

I. INTRODUCTION

Nickel(II) complexes containing mixed N/O donor Schiff base ligands and a variety of bridging polyatomic anions (e.g. N_3^-, NO_2^-, SCN^- , $RCOO^-$etc.) constitute an interesting research area in chemistry. Such polynuclearNi(II) complexes have received considerable attention due to their potential applications in the field of biological systems [1], catalysis [2] and magnetism [3]. One of the most interesting aspects of the chemistry of Ni(II) with tridentate NNO donor Schiff base ligands is that a small variation in the diamine and/or the carbonyl compound from which the Schiff base is derived can bring about significant variations in the coordination geometry [4]. If an NNO donor Schiff base and a polyatomic bridging moiety are present together in a complex then it is very difficult to predict its structure. In such cases there are too many factors that should be taken into consideration.So these type of NNO donor Schiff base ligands along with variouspolyatomic anions are an excellent combination to produce not only various structural architectures [5]. A CSD search shows that there are somanyNi(II) complexes containing different tridentate NNO donor Schiff base ligands in conjugation with various anionic coligands. Among them nearly forty are mononuclear complexes where the secondary amine group of the ligand either coordinates to the metal centre or remains pendant. Most of these mononuclear complexes are square planar [6] and only a few are octahedral [7]. Usually, the weakly coordinating anions, e.g. Cl, ClO_4,NO_3etc, present as counter ions in the square planar complexes, and strongly coordinating azide or thiocyanate ligands in the octahedral complexes coordinate to the two axial positions.

In this present paper, we have synthesized a new nickel(II)complex with a NNO donor tridentate Schiff base ligand derived from N,N-dimethyl-1,2-ethylenediamine and salicylaldehyde. The complexis characterized by X-ray crystallography and spectroscopy analyses. Structural analysis show that complex **1**isdinuclear, bridged by both μ_2-phenoxido and hydroxoligands.Here one Ni(II) centre is square planar and the other is octahedral.

Experimental section

Starting materials

N,N-Dimethyl-1,2-ethanediamine and salicylaldehyde were purchased from Lancaster and were of reagent grade. They were used without further purification.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Very small amount of material should be prepared and it must be handled with care.

Synthesis of the Schiff base ligand 2-[(2-dimethylaminoethylimino)-methyl]-phenol (HL)

The tridentate Schiff base ligand was prepared by the condensationof salicylaldehyde (1.0 mL, 10 mmol) and N,N-dimethylethane-1,2-diamine (1.1 mL, 10 mmol) in methanol (20 mL) underreflux for 1 h. The resulting dark yellow solution was then used directlyfor complex formation.

Synthesis of complex$[Ni_2L_2(OH)(OH_2)]ClO_4\cdot CH_2Cl_2$ (1)

$Ni(ClO_4)_2\cdot 6H_2O$ (1.331 g, 5 mmol), dissolved in 10 mL of methanol,was added to a methanolic solution (15 mL) of the ligand (HL)(5 mmol) with constant stirring. The color of the solution turnedgreen. By slow evaporation of the resulting solution at room temperature,grassy green crystalline solids were obtained after 24 hours.It was filtered and dissolved in aminimum volume of dichloromethane. By slow diffusion of thesolution in n-hexane, blocked shaped greencolored crystals ofcomplex **1** appeared after several days which were suitable forX-ray analysis.

Physical Measurements

IRspectra in KBr pellets (4500-500 cm-1) were recorded using a Perkin-Elmer RXI FT- IRspectrophotometer. Electronic spectra (800-220 nm) was recorded in a Hitachi U-3501 spectrophotometerin acetonitrile solution.

Crystal data collection and refinement

6289 independent data werecollected with MoKα radiation of complex**1** at room temperature using the OxfordDiffraction X-Calibur CCD System.Crystal data for the complex**1**are given in Table 1. A crystal of the complex was positionedat 50 mm from the CCD. 321 frames were measured with a counting time of 10s. Data analysis was carried out with the CRYSALIS program. [8] The structures were solved using direct methods with the SHELXS97 program [9]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In the structure, hydrogen atoms bonded to oxygen were readily located in difference Fourier maps and refined with distance constraints. An empirical absorption correction for **1** was carried out using the ABSPACK program [10]. In complex **1**, there is a disordered perchlorate and a disordered dichlormethane solvent molecule. The structure was refined on F^2using SHELXL97to R1 0.0676; wR2 0.2040 for 4653 data with $I>2\sigma(I)$.

Table 1. Crystal data of the complex**1**

	1
Formula	$C_{23}H_{35}Ni_2N_4O_8Cl_3$
Formula wt.	719.32
Space group	*C2/c*
Crystal system	Monoclinic
a / Å	32.587(3)
b / Å	11.816(1)
c / Å	19.975(2)
α =γ / deg	90
β / deg	126.511(2)
V / Å^3	6182.0(9)
Z	8

d_{cal} (g.cm^{-3})	1.546
μ (mm^{-1})	1.527
R_{int}	0.0497
No. of unique data	6289
Data with I>2σ(I)	4653
R1 on I>2σ(I)	0.0676
wR2 on I>2σ(I)	0.2040
Gof Value	1.069

II. RESULTS AND DISCUSSION

Syntheses, IR and UV-Vis spectra of the complexes

The mono-condensed tridentate Schiff base ligand HL and itshydroxo-bridged, methoxobridged and azido-bridged dinuclearcomplexes with the Fe(III) ion and two Ni(II) complexes with anionic chloride and nitrate co-ligands have been reported by us[41,42]. In all of the cases metal ions are hexa-coordinated. In the present investigation we have used this ligandfor the synthesis of a new Ni(II) complex with anionic perchlorateco-ligand. The complex has been prepared in asimple way: the tridentate ligand HL was allowed to react withthe respective Ni(II) salt in a 1:1 molar ratio in methanol mediumat room temperature. The structure and composition of theresulting compound is, however, very different. The dinuclear complex with two Ni(II) atoms are showing different geometries. One is octahedral and another one is square planar.

In the IR spectra of complex **1**, a strong and sharp band due to azomethine $\bar{\upsilon}$(C=N) appears at 1625 cm^{-1}. The appearance of a broad band near 3297 cm^{-1} indicates the presence of water molecule,as substantiated by their crystal structures. The sharp peakat 1118 cm^{-1} gives evidence for the presence of ionicperchlorate anion.

The UV-Vis spectra of the compound **1,** is recorded in methanol solution at room temperature. The electronic spectrashow d–d absorption bands at 582 and 885 nm for compound **1**. These bands are assignedto the spin allowed transitions $^3A_{2g}\rightarrow T_{1g}$(F) and $^3A_{2g}\rightarrow {}^3T_{2g}$,respectively. The higher energy d–d bands are masked by strongligand to metal charge-transfer transitions.

Description of the structures

The structure of the complex **1** contains a discrete $[Ni_2L_2(OH)(OH_2)]^+$ cation together with a disordered perchlorate anion and a disordered dichloromethane solvent molecule. The cation is shown in Figure 1. Here Ni-A has a four-coordinate square planar environment while Ni-B has a six-coordinate octahedral environment. Ni-A is bonded to the three donor atoms of ligand **L** together with a hydroxide O(2). Both O(11A) and O(2) bridge between Ni-A and Ni-B. In addition to these two atoms, Ni-B is also bonded to the three donor atoms of a second ligand **L** and a water molecule.

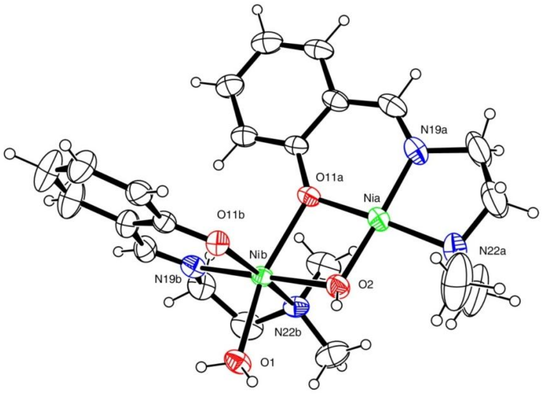

Figure 1. The structure of the $[Ni_2L_2(OH)(OH_2)]^+$ cation with ellipsoids at 30% probability.

As expected the bond lengths around the four-coordinate Ni-A are significantly shorter than those around the six-coordinate Ni-B. Thus to the ligand Ni-A distances are 1.861(4)Å to O(11A), 1.848(5)Å to N(19A) and 1.943(5)Å to N(22A). These can be compared to distances from Ni-B, namely 2.034(3)Å to O(11B), 2.020(4)Å to N(19B) and 2.205(4)Å to N(22B). A similar pattern is observed in distances to the bridging hydroxide O(2) with a distance to Ni-A of 1.842(4)Å compared to 1.989(4)Å to Ni-B. Other distances involving Ni-B are 2.119(4)Å to the water molecule O(1) and 2.188(3)Å to the bridging O(11A). The geometry around Ni-B is significantly distorted from octahedral presumably due to the proximity of Ni-A and the presence of two bridging atoms in the coordination sphere. However the equatorial planes around Ni-A and Ni-B are closely planar with an r.m.s. of0.062Å of O(1), O(2), N(19B), O(31) around Ni-B which is 0.028(2)Å from the plane and an r.m.s. of 0.061Å for O(2), O(11A), N(19A), N(22A) around Ni-A which is 0.031Å from the plane.

The coordinated water molecule O(1) forms hydrogen bonds, H(1) to a perchlorate oxygen atom O(71) and H(2) to O(11) from an adjacent molecule with symmetry element 0.5-x, 1.5-y, 1-z. Dimensions are H(1)...O(71) 2.13, O(1)-H(1)...O(71) 147^{o}, O(1)...O(71) 2.868(7)Åand H(2)...O(11) 1.89Å, O(1)-H(1)...O(11) 158^{o} and O(11)...O(71) 2.936(5)Å.

Table 2. Bond distances and angles around the metal centers in complex **1**

Atoms	**Distance (Å)**	**Atoms**	**Distance (Å)**
NiA – O(2)	1.842(4)	NiA – O(11A)	1.861(4)
NiA – N(19A)	1.848(5)	NiA – N(22A)	1.943(5)
NiB – O(2)	1.989(4)	NiB – O(1)	2.119(4)
NiB – N(19B)	2.020(4)	NiB – O(11A)	2.188(3)
NiB – O(11B)	2.034(3)	NiB – N(22B)	2.205(4)
Atoms	**Angle (°)**	**Atoms**	**Angle (°)**
O(2) - NiA - N(19A)	177.3(2)	O(2) - NiA - N(22A)	95.1(2)
O(2) - NiA - O(11A)	83.35(16)	N(19A) - NiA - N(22A)	86.9(2)
N(19A) - NiA - O(11A)	94.8(2)	O(11A) - NiA - N(22A)	174.18(19)
O(2) - NiB - N(19B)	174.61(17)	N(19B) - NiB - O(1)	92.29(16)
O(2) - NiB - O(11B)	95.06(15)	O(11B) - NiB - O(1)	89.96(14)
N(19B) - NiB - O(11B)	90.01(16)	O(2) - NiB - O(11A)	72.07(14)
O(2) - NiB - O(1)	89.55(15)	N(19B) - NiB - O(11A)	106.27(15)
O(11B) - NiB - O(11A)	88.94(13)	O(11B) - NiB - N(22B)	172.25(16)
O(1) - NiB - O(11A)	161.40(14)	O(1) - NiB - N(22B)	90.93(15)
O(2) - NiB - N(22B)	92.64(17)	O(11A) - NiB - N(22B)	92.65(14)
N(19B) - NiB - N(22B)	82.27(18)		

III. CONCLUSIONS

In the present study we have synthesize and characterize a dinuclearNi(II) complex from N,N-Dimethyl-1,2-ethanediamine and salicylaldehyde. Crystal structure analysis shows that two metal atoms consists two different coordination environment, which is quite unique among such type of ligand (Schiff base) and coligands. Two differentphenoxido and hydroxo bridging modesare present in the complex.

ACKNOWLEDGMENTS

Thank you to Department of Chemistry, SushilKar College, Champahati, Baruipur, South 24 parganas,West Bengal, India.

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