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Synthesis and characterisation of ammonium mediated assembly of two neutral nickel(II) Schiff base fragments

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1. Introduction

Current research in the field of supramolecular chemistry has shown that small building blocks can lead, through self-assembly processes, to large, well-defined structures, which are held together by non-covalent interactions such as hydrogen bonds [1,2]. In the design and synthesis of multidentate ligands competent of participating in complicated molecular structures upon complexation, in pre-arranged manners, with transition metals, have also been done successfully [3-5]. Many examples of these types of ligands were provided by the Salen family of Schiff bases, which coordinate to various kinds of transition and typical metals to give stable compounds, some of which are frequently used as catalysts [6-8], models of metalloenzymes [9,10], NLO materials [11,12] and building blocks for interlocked molecules [13]. Transition metal compounds of tetradentate Schiff bases can also act as chelating agents towards both transition [14-18] and non-transition metal ions [19-22] including alkali [23-28] and alkaline earth metals [29,30]. Among them, investigation on the compounds containing the alkali metal/ammonium ions is of utmost interest in connection with a more comprehensive view of the chemistry of d^o cations and with the influence of positive charges on the electronic properties of the transition-metal centre.

Interestingly, reports of the preparation of 3d/ammonium ion compounds are relatively scanty and best to our knowledge, only three such compounds are found in the literature [31–33]. All the

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ABSTRACT

The 1:2 condensation of *o*-phenelenediamine and *o*-vanilline yields a compartmental N₂O₄ ligand *N*,*N*⁻(1,2-Phenylene)-bis(3-methoxysalicylideneimine) [H₂L]. When nickel(II) thiocyanate is added to the methanol solution of H₂L, followed by addition of ammonium thiocyanate, an unusual nickel(II) compound, [NH₄(NiL)₂SCN]·H₂O (**1**), is separated out in which an ammonium ion is sandwiched between two neutral square planner NiL moieties. Hydrogen bonding interactions are observed among the ammonium ion, NiL moieties, the thiocyanate anion and the water of crystallization. The compound is characterized by C, H, N analysis, UV–VIS and IR spectroscopy, room temperature magnetic susceptibility measurement and X-ray crystal diffraction study. The compound crystallizes in monoclinic space group $P2_{1/n}$ with a = 13.8636(7) Å, b = 14.0267(7) Å, c = 22.2715(10) Å and $\beta = 94.301(3)^\circ$.

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three compounds use nickel salen to trap ammonium ion. No report of the preparation of 3d/ammonium compounds with salphen 1:2 condensation product of o-phenylenediamine and salicylaldehyde or substituted salphen is found in the literature, probably due to the relative instability of the compounds caused by the enhanced rigidity imposed to ligand by the *o*-phenelenediamine moiety. Our attempts with H₂L [*N*,*N'*-(1,2-Phenylene)-bis (3-methoxysalicylideneimine)] furnished for the first time, ammonium sandwiched compound with such sterically strained ligand. X-ray crystal structure determination of it has established the structure. Herein, we report the facile synthesis, spectroscopic characterisation, and magnetic property of [NH₄(NiL)₂SCN]-H₂O (**1**).

2. Experimental

Nickel(II) thiocyanate was prepared following the method reported in the literature [34]. All other starting materials were commercially available, reagent grade, and used as purchased without further purification.

2.1. Synthesis

2.1.1. Preparation of the ligand (H_2L)

The ligand H_2L was synthesized by refluxing a methanol solution of *o*-phenylenediamine (108 mg, 1 mmol) and *o*-vanilline (304 mg, 2 mmol) in 1:2 molar ratios for 1 h. It was not isolated and used directly for the preparation of the compound.



Note



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Table 1Crystal data and refinement details.

Formula	C45H42N6Ni2O9S
Formula weight	960.30
Crystal size (mm)	$0.2\times0.2\times0.2$
Temperature (K)	293
Crystal system	monoclinic
Space group	$P2_{1/n}$
a (Å)	13.8636(7)
b (Å)	14.0267(7)
c (Å)	22.2715(10)
α (°)	90
β (°)	94.301(3)
γ (°)	90
Z	4
$d_{\rm calc}$ (g cm ⁻³)	1.477
$\mu (\text{mm}^{-1})$	0.984
F(000)	1992
Total reflections	65663
Unique reflections	10025
Observed data $[I > 2\sigma(I)]$	5649
No. of parameters	582
R _{int}	0.057
R_1, wR_2 (all data)	0.1174 and 0.2185
$R_1, wR_2 [I > 2\sigma(I)]$	0.0614 and 0.1913

2.1.2. Preparation of compound $[NH_4(NiL)_2SCN] \cdot H_2O(1)$

A methanol solution (10 ml) containing Ni(SCN)₂·4H₂O (247 mg, 1 mmol) and NH₄SCN (76 mg, 1 mmol) was added to a methanol solution (20 ml) of the ligand, H₂L (1 mmol) under reflux. Red crystalline compounds started to separate immediately. Red pallet-like single crystals of **1**, suitable for X-ray diffraction, were obtained from acetonitrile solution. Yield: 340 mg (70.81%, based on Ni(II) salt). *Anal.* Calc. for C₄₅H₄₂N₆Ni₂O₉S: C, 56.28; H, 4.41; N, 8.75. Found: C, 56.3; H, 4.4; N, 8.7%. UV/Vis (DMF): $\lambda_{max}(nm)$ (ε_{max} , dm³ mol⁻¹ cm⁻¹) = 486 (986), Magnetic moment *diamagnetic.*

2.2. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin–Elmer 240C elemental analyzer. IR spectrum in KBr (4500–500 cm⁻¹) was recorded using a Perkin– Elmer RXI FT-IR spectrophotometer. Electronic spectrum in DMF (1200–350 nm) was recorded in a Hitachi U-3501 spectrophotometer. The magnetic susceptibility measurement was done with an EG and PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants.

2.3. X-ray crystallography

Single crystals having suitable dimensions were used for data collection by means of a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 , using the SHELX-97 package [35]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms of the water molecule of crystallization and that of ammonium ion were located by difference Fourier maps and were kept at fixed positions. Other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on the atoms to which they are attached. Empirical absorption corrections were carried out with the ABSPACK program [36]. The structure was refined to $R_1 = 0.0614$ and $wR_2 = 0.1913$, for 5649 reflections with $I > 2\sigma(I)$. The crystallographic and refinement data are summarized in Table 1. Selected

bond lengths and bond angles are shown in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Synthesis

The ligand was prepared by the 1:2 condensation of the *o*-phenylenediamine with *o*-vaniline in methanol following the literature method [37]. The ligand was then refluxed with a mixture of nickel(II) thiocyanate and ammonium thiocyanate to prepare compound **1**, where an ammonium ion is stacked between two NiL units and the charge is satisfied by the thiocyanate (Scheme 1). In absence of the ammonium thiocyanate, a different compound NiL was formed, the structure of which is reported elsewhere [38]. The compound can also be prepared by stirring a methanol solution of NiL with ammonium thiocyanate. Ammonium ion mediated assembly of neutral Ni(II) Schiff base compound is not very common in the literature. No examples of this these types of compounds are found in the literature with H₂L or any compartmental Schiff bases.

3.2. Spectroscopic and magnetic properties

In the IR spectrum of compound **1**, distinct band due to the azomethine (C=N) group at 1603 cm⁻¹ is customarily noticed [39–41]. A broad band around 3460 cm⁻¹ is assigned to the OH stretching vibration of the water molecule, which is involved in hydrogen bonding [42]. The electronic spectrum shows one absorption band in the visible region at 486 nm. A lack of any electronic transition at longer wavelengths indicates a large crystal-field splitting and is consistent with the square planar geometry of Ni(II) compounds [43]. However, there are many high intensity absorption bands in the UV region indicating LMCT transitions.

Room temperature magnetic susceptibility measurement shows that the compound is diamagnetic, thereby indicating the presence of magnetically non-couple square planer nickel(II) ions.

Table 2 Coordination environment around Ni(II).					
1.847(3)					
1.843(3)					
1.842(4)					
1.846(4)					
1.845(3)					
1.844(3)					
1.849(4)					
1.839(4)					

Table 3	
Selected bond angles around Ni(II).	

O(2)-Ni(1)-O(3)	84.40(13)
O(2)-Ni(1)-N(1)	95.18(14)
O(3)-Ni(1)-N(2)	94.62(16)
N(1)-Ni(1)-N(2)	85.87(17)
O(2)-Ni(1)-N(2)	178.06(14)
O(3)-Ni(1)-N(1)	177.77(13)
O(6)-Ni(2)-O(7)	83.96(13)
O(6)-Ni(2)-N(3)	178.42(16)
O(7)-Ni(2)-N(4)	178.48(14)
N(3)-Ni(2)-N(4)	85.54(17)
O(6)-Ni(2)-N(4)	95.44(15)
O(7)-Ni(2)-N(3)	95.09(15)



Fig. 1. View of compound 1 with 20% ellipsoid probability. Only the relevant hydrogen atoms are shown.

3.3. Structure description

The structure of **1**, as shown in Fig. 1, shows that ammonium ion is surrounded by two molecules of NiL moieties. The mean values of the bond lengths and angles in the [NiL] moieties are in fairly

good agreement with those found previously in similar compounds [31,38]. The two Ni atoms are both four-coordinated in an approximately square-planar geometry constructed by two imine N atoms and two phenolate O atoms from Salen-type Schiff base ligand (H₂L). Sum of the different angles around the Ni(1) and

Table 4

Hydrogen bond distances (Å) and angles (°).

D–H…A	D-H	D…A	Н…А	D-H…A
N(6)-H(101)N(5)	1.02(7)	2.940(8)	1.95(7)	162(6)
N(6)-H(103)O(3)	0.62(5)	2.973(7)	2.42(5)	150(6)
N(6)-H(100)O(6)	1.07(7)	2.966(6)	2.38(7)	113(4)
N(6)-H(100)O(7)	1.07(7)	2.920(6)	1.86(7)	171(6)
N(6)-H(102)O(1)	0.75(5)	2.962(7)	2.27(5)	154(5)
N(6)-H(102)O(2)	0.75(5)	2.944(6)	2.37(6)	135(5)
O(9)-H(106)O(5)	0.99(7)	3.160(8)	2.21(7)	163(5)

Ni(2) atoms are 360.03° and 360.07° respectively, indicating square-planer geometry around the Ni atoms. O(2)-Ni(1)-N(1). N(2)-Ni(1)-O(2), O(6)-Ni(2)-N(3), O(7)-Ni(2)-N(4) angles are found to be 178.06(14)°, 177.77(13)°, 178.42(16)° 178.48(14)°, respectively. Deviations of the coordinating atoms O(2), O(3), N(1) and N(2) from the least-square mean planes through them are -0.031(3), 0.031(3), 0.031(3), -0.031(3)Å, respectively, whereas the deviations of the coordinating atoms O(7), O(6), N(3) and N(4) from the least-square mean planes through them are -0.021(3), 0.021(3), 0.021(4), -0.021(3) Å, respectively. The dihedral angle between the mean planes passing through [N(1)-N(2)-O(2)-O(3)] and [N(3)-N(4)-O(6)-O(7)] is 3.93° , suggesting that the two sets of L^{2-} are almost parallel. The intra-molecular separation between Ni(1)...Ni(2) is 3.734 Å, which does not imply any metal-metal bonding between the nickel atoms. The angle between the planes passing through [Ni(1)-Ni(2)-O(3)] and [Ni(1)-Ni(2)-O(7)] is 45.38° which shows that the two NiL units are in staggered geometry.

Hydrogen bonding interactions are observed among the ammonium ion, NiL moieties, the thiocyanate anion and the water of crystallization (Table 4). Of the four hydrogen atoms attached with N(6), H(101) and H(103) form strong H bond with N(5) of the thiocyanate and O(3) of the NiL moiety, respectively. The other two H atoms, H(102) and H(100), form strong bifurcated hydrogen bonds with two oxygen atoms, O(1), O(2) and O(6), O(7) of the two different [NiL] moieties, respectively. H(106) from the water of crystallization forms strong H-bond with O(5). The H-bonding network is shown in Fig. 1.

4. Conclusion

The isolation and crystal structure determination of the ammonium mediated assembly of two NiL fragments, $[NH_4(NiL)_2SCN]$, unambiguously shows for the first time that the salen type compartmental Schiff base, *N*,*N'*-(1,2-Phenylene)-bis(3-methoxysalicylideneimine) can be used to trap ammonium ions. Thus it opens up new possibilities for the synthesis of such type of compounds.

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Appendix A. Supplementary data

CCDC 805838 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc. cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2011.08.026.

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