

Synthesis, X-ray structural characterization and solution studies of a mononuclear Ni(II)-Schiff base complex bearing free formyl groups

Shankareswar Gupta, Anangamohan Panja, Nizamuddin Shaikh, Sanchita Goswami & Pradyot Banerjee*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India

E-mail address: icpb@mahendra.iaes.res.in; Fax No.: 91-33-2473 2805

and

Ray J Butcher

Department of Chemistry, Howard University, 2400 Sixth Street, NW, Washington, DC 20059, USA

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A new mononuclear Ni(II)-Schiff base complex has been synthesized and structurally characterized through X-ray crystallography. The compound crystallizes in the monoclinic space group C2/c (No. 15) with $a = 17.268(7)$, $b = 14.619(6)$ and $c = 10.683(4)$ Å. The molecular structure shows that the Ni(II) ion is in the distorted octahedral environment in which two phenolic oxygen atoms occupy the axial positions. Two -CHO groups arising out of the 2,6-diformyl-4-methylphenol remain as pendants. UV/vis and cyclic voltammetric experiments have been performed of the Ni(II) complex in DMF solution and the results compare well with the previously reported systems.

2,6-Diformyl-4-methylphenol (dfp) has been proved to be the potential precursor for the synthesis of mono- and multi-nucleating metal complexes over the years¹⁻¹². The condensation of dfp and the diamines in the presence of 3d metals have resulted in homo- and hetero-dinuclear complexes. The metal-metal cooperative effects and consequent physico-chemical and biocatalytic properties of these complexes have been studied in detail^{13,14}. Efforts to prepare metal free ligands (acyclic and macrocyclic) by the condensation of dfp and amines have resulted mostly in the polymeric and oligomeric products, though in some cases free ligands have been isolated^{15,16}. Most of the template syntheses using this precursor have produced symmetrical macrocyclic complexes. Recently, Korupoju *et al.*¹² reported the isolation of a mononuclear acyclic manganese(III) complex prepared by the condensation of dfp and chiral diamine which bears two free formyl groups. Though dfp and the diamines have been successfully exploited to prepare a lot of homo- and hetero-metallic polynuclear complexes, the uses of polyamines have not so far been attempted to that extent. The less use of polyamine is due to the inability to control the unwanted polymeric and/or oligomeric intractable products. We have successfully exploited the polyamines [e.g. N,N'-bis(3-aminopropyl)-ethylenediamine and triethylenetetramine] to synthe-

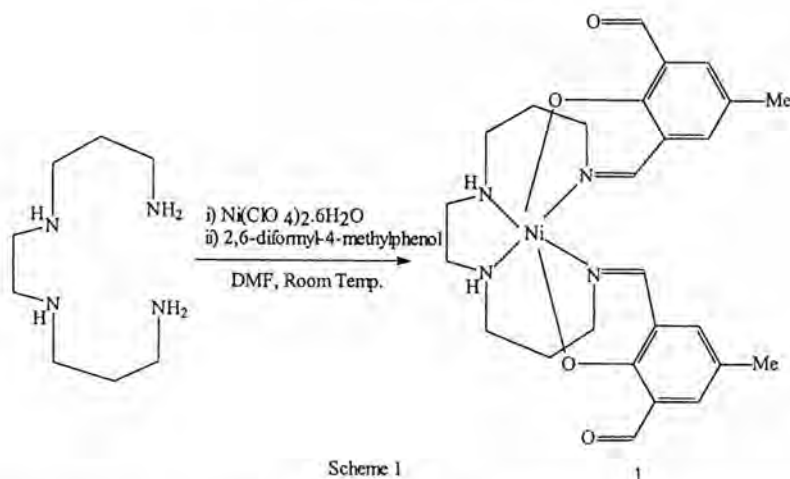
size a series of Mn(III) complexes having N₄O₂ donor set by the condensation of these amines and substituted salicylaldehyde by the metal template method^{17,18}. In an effort to explore the reactivity of these amines towards the dfp, we could isolate an acyclic mononuclear Ni(II) complex having N₄O₂ donor set which bears two free formyl groups. In this paper we present the synthesis, structural characterization and solution properties of complex **1** (Scheme 1).

Materials and Methods

All the chemicals including N,N'-bis(3-aminopropyl)-ethylenediamine, *p*-cresol, paraformaldehyde, hexamethylenetetramine, CH₃COOH, H₂SO₄, HClO₄, CH₃OH and DMF were of analytical reagent grade. Ni(ClO₄)₂·6H₂O was prepared by dissolving NiCO₃·2Ni(OH)₂·4H₂O in aqueous perchloric acid. 2,6-diformyl-4-methylphenol was prepared following the published procedure¹⁹.

Synthesis of complex **1**

To a DMF solution (30 cm³) of N,N'-bis(3-aminopropyl)-ethylenediamine (5 mmol, 0.9 g) was added a DMF solution (10 cm³) of Ni(ClO₄)₂·6H₂O (5 mmol, 1.82 g) with stirring at room temperature. To the resulting mixture was added slowly a DMF solu-



tion of 2,6-diformyl-4-methylphenol (10 mmol, 1.66 g) with stirring magnetically. The solution was further stirred for an hour and then filtered to remove any suspended particles. The resulting brown-red solution was allowed to stand for 3-4 days whereby brown-red crystals of **1** were formed. The compound was filtered, washed with diethyl ether and dried in air. Yield = 75 % based on $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ used. Anal. Cal for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_4\text{Ni}$; C, 59.6; H, 6.1; N, 10.7%. Found, C, 60.1; H, 6.0; N, 10.6%.

Physical measurements

Microanalysis (CHN) was performed in a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Nicolet, MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Cyclic voltammetry (scan rate of 0.05 V s^{-1}) was performed at a platinum electrode using an EG&G PARC electrochemical analysis system (model 250/5/0) in DMF under dry nitrogen atmosphere in conventional three electrode configurations. Spectral measurements were performed in an UV-vis spectrophotometer (UV-2100, Shimadzu, Japan) equipped with thermostated cell compartments.

Crystal structure determination and structural refinements of complex **1**

A suitable single crystal of dimension $0.3 \times 0.3 \times 0.2 \text{ mm}^3$ of **1** was mounted on an automatic Bruker P4 diffractometer equipped with a graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell dimensions and intensity data were measured at 296 K. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for non-hydrogen atoms using Bruker SHELXTL (data reduction),

Table 1—Data collection and structure refinement of complex **1**

Empirical formula	$\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_4\text{Ni}$
Formula weight	523.25
Crystal system	Monoclinic
Space group	C2/c (No. 15)
$a / \text{\AA}$	17.268(7)
$b / \text{\AA}$	14.619(6)
$c / \text{\AA}$	10.683(4)
$\beta / ^\circ$	112.172(10)
$V / \text{\AA}^3$	2497.71(17)
Z	4
$D(\text{calc}) [\text{g/cm}^3]$	1.391
$\mu(\text{Mo-K}\alpha) / \text{mm}^{-1}$	0.816
$F(000)$	1104
Crystal size / mm	$0.30 \times 0.30 \times 0.20$
Temperature / K	93
$\lambda(\text{Mo-K}\alpha) / \text{\AA}$	0.71073
Theta Min-Max / $^\circ$	1.9–28.3
Total data	9758
Unique data (R_{int})	3082 (0.038)
Observed data [$I > 2.0 \text{ sigma}(I)$]	2700
Final R_1, wR_2 [$I > 2 \text{ sigma}(I)$]	0.0282, 0.0776

SHELXS²⁰ (structure solution) and SHELXL²¹ (structure refinement). The hydrogen atoms were included in structure factor calculations in their idealized position. Informations concerning crystallographic data collection and refinement of the structures are compiled in Table 1.

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 209477. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK [Fax: (internet.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

Structure of complex **1**

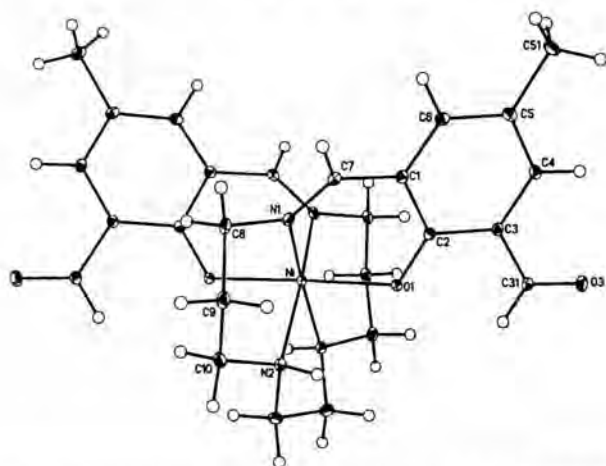
Suitable single crystals of **1** were obtained as DMF solvates and taken directly from its mother liquor. The molecular structure of **1** incorporating the atoms labeling scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 2. The metal ion is in the hexadentate distorted NiN_4O_2 fashion. The in-plane positions are occupied by four N atoms of the Schiff base ligand having Ni-N1 (imine) bond length = 2.0533(12) Å and that of Ni-N2 (amine) = 2.1132(12) Å. Phenolic oxygen atoms are in a *trans*-configuration in the complex. Both the Ni – O bond lengths are identical [2.0421(11) Å] and the (O1-Ni-O1a) angle is 178.37(4)°. The two coordinating ONN halves are facial. The structural features are thoroughly consistent with those reported for Ni(II)-Schiff base complexes²²⁻²⁴. The crystal lattice is stabilized by extensive hydrogen bonding which is revealed through the molecular packing diagram (Fig. 2). The

intermolecular hydrogen bonding involves the free –CHO oxygen of one molecule and the amine proton (N-H) of the neighboring molecule [N(2) – H(2A)---O(3) = 3.0532(18) Å].

UV/vis and IR spectroscopy

The UV/vis spectrum of complex **1** is characterized by a very weak band in the range 750 – 900 nm having $\lambda_{\text{max}} = 840$ nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = 40$) and an intense band in the 380–500 nm range with $\lambda_{\text{max}} = 448$ nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = 18,760$) in DMF. In DMSO the UV/vis spectral features of **1** are almost identical but with a little difference in intensity of the corresponding bands probably due to the solvent effects. The low intensity band at 840 nm is due to the *d-d* transition, consistent with the previously reported Ni(II) complexes in octahedral environments²²⁻²⁴. The intense band at 448 nm may be attributed to the ligand to metal charge transfer (LMCT).

The IR spectrum of **1** is depicted by an intense sharp band at 1650 cm^{-1} due to the free –CHO group. The bands due to (C=N) of the Schiff base ligand appear at 1620 cm^{-1} . The other main bands in IR spec-



trum are observed at 1630, 1384, 1479, 1289, 1229 and 960 cm^{-1} .

Electrochemical studies

Cyclic voltammograms of the Ni(II) complex was recorded in DMF solution with TEAP as supporting electrolyte in the potential range -1.5 to $+1.5$ V. The spectrum is characterized by a well-defined reversible oxidation wave with $E_{1/2} = 0.40$ V (Fc/Fc^+) and $\Delta E = 0.07$ V and illustrated in Fig. 3. The anodic process corresponds to the Ni(II)/Ni(III) couple and the peak-to-peak separation is that expected for an electrochemically one electron reversible process. The oxidation potential is much lower shifted compared to the corresponding N_2O_2 Schiff base ligand complex²⁴. It is, however, not surprising as the oxidation potentials are markedly dependent on the ligand environment and the observation made here suggests the better stabilization of Ni(III) species in the present chemical environment²⁴.

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