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Synthesis, spectral, thermal and electrochemical studies of nickel (II) complexes with N_2O_2 donor ligands

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Abstract

The free Schiff base ligands H_2MABCE, H_2MABCP, and H_2MABCT and their complexes [Ni(MABCE)], [Ni(MABCP)], and [Ni(MABCT)] have been synthesized and characterized by spectroscopic and cyclic voltammetric studies. The coordination geometry around the nickel atom is a square planar with N_2O_2 donor atoms. Cyclic voltammetric studies of the complexes show one electron quasi-reversible waves corresponding to Ni(II)/Ni(I) and Ni(II)/Ni(III) processes. The electronic spectra of the complexes reveal a four coordinate geometry. The crystal structure of one of the ligands (H_2MABCE) has also been reported.

Keywords: Schiff bases; Nickel (II) complexes; Crystal structure; Cyclic voltammetry

The Schiff base compounds constitute an important class of ligands which have been extensively studied in coordination chemistry mainly due to their facile synthesis and easily tunable steric, electronic, and catalytic properties. They are also useful in constructing supramolecular structures [1–3]. The condensation of aldehyde-bearing coordinating groups with amino acids and peptides provides interesting Schiff bases, used to make a combinatorial library of ligands [4]. On the other hand, complexes of chromium, manganese, nickel and ruthenium with a wide variety of Schiff bases having donor atoms such as N_2O_2 and N_4 around the metal ion have been used as catalysts for carbonylation, hydrogenation, hydroformylation and epoxidation reactions [5,6]. The cobalt (II) and manganese (II) complexes with tetradentate Schiff base ligands which coordinate through N_2O_2 donor atoms have been extensively studied as oxygen-carriers and also as catalysts for water splitting system [7,8]. Schiff base complexes are also known for their significant biological activities such as photosynthesis and transport of oxygen in mammalian and other respiratory systems [9,10].

The synthesis and studies of Schiff base ligands and their Ni(II) complexes viz. [Ni(MABCE)], [Ni (MABCP)], and [Ni(MABCT)] have been described in the present communication. The aliphatic diamines such as diaminoethane, 1,2-diaminopropane, and 1,3-diaminopropane were condensed with two equivalents of 2-hydroxy-4-methacryloyloxy benzaldehyde to form ligands with Schiff base functionalities (Scheme 1) [11]. The ligands H_2MABCE, H_2MABCP and H_2MABCT dissolved in acetonitrile were allowed to evaporate slowly for five days to form greenish yellow crystals. The complexes [Ni(MABCE)], [Ni(MABCP)], and [Ni(MABCT)] were obtained by the reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ with ligand in ethanol in the mole ratio 1:1 (Scheme 2) [12]. The ligands were characterized by IR, EI-mass, ^{1}H NMR and UV–vis spectral analysis.

The infrared spectra of Schiff base ligands H_2MABCE, H_2MABCP and H_2MABCT show υ(C=N) vibration at 1621–1635 cm^{-1} [13] and the strong broad band at 3300–3400 cm^{-1} is attributed to phenolic OH group [14]. The ^{1}H NMR spectra of the ligands exhibit

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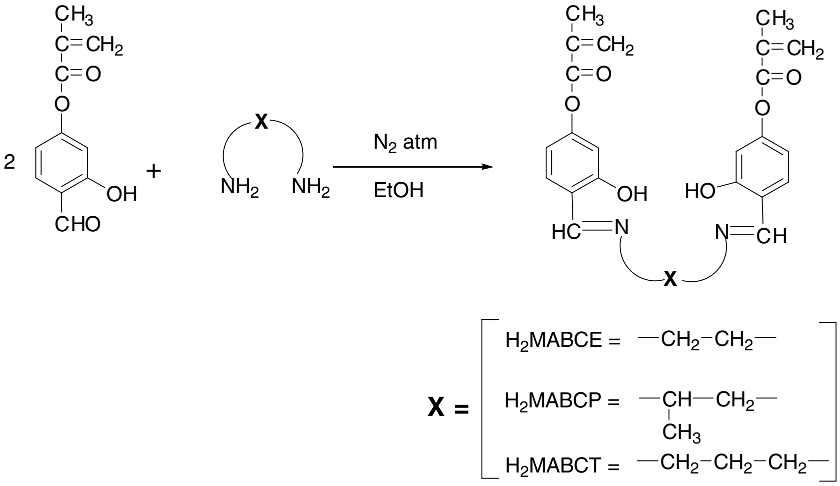
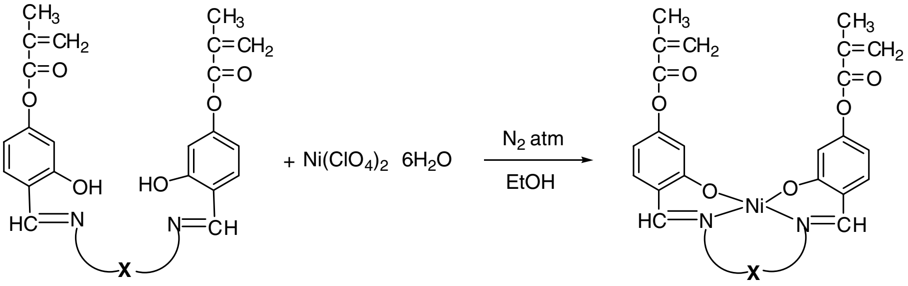


Scheme 1. Synthesis of Schiff base ligands.



Scheme 2. Synthesis of Schiff base nickel (II) complexes.

resonances corresponding to >CH=N, aliphatic methyl, methylene, methine, vinylic and aromatic protons [15]. The structure of the ligand H_2MABCE was solved by X-ray analysis [16] and its ORTEP plot is shown in Fig. 1. The aliphatic methylene diimine bridge is in trans conformation having crystallographically equivalent two 2-hydroxy-4-methacryloyloxy benzaldehyde moieties, and a two fold centre of inversion is present in between C-12 and C-12a carbon atoms. During complexation the ligand undergoes a conformational change and is converted into *cis* form [17,18]. The relevant crystallographic data are summarized.[1]

The infrared spectra of Ni(II) complexes exhibit typical bands observed in the case of free ligands. The strong peak assigned to υ(C=N) is observed in the region 1610–1620 cm^{-1}. The azomethine frequency of the complexes undergoes a negative shift by about 10–15 cm^{-1} when compared to the free ligands. This may be attributed to the coordination of the azomethine nitrogens to the metal ion. The absence of phenolic OH frequency at 3300–3400 cm^{-1} is due to deprotonation of phenolic oxygen and its subsequent coordination with the metal ion [19,20].

The electronic spectra of the complexes were recorded in DMF medium and the relevant data are provided in [12]. The nickel (II) complexes exhibit four bands. The low intensity band observed at 532–550 nm ($\varepsilon = 240$–$260\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) is attributed to d–d transition ($^1A_{1g} \rightarrow {}^1A_{2g}$) of the metal ion, which indicates a square planar geometry around the metal ion. The LMCT band at 390–403 nm, ($\varepsilon = 1600$–$1940\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) can be attributed to N → Ni charge transfer, while the third band at 306–315 nm, ($\varepsilon = 3490$–$5340\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) is also due to LMCT arising out of O → Ni charge transfer. The band observed at 263–270 nm ($\varepsilon = 13{,}480$–$15{,}500\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) may be due to a ligand localized transition [21,22]. The VSM measurement indicates that

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[1] *Crystal and experimental data for ligand H_2MABCE*: $C_{24}H_{24}N_2O_6$: $M = 436.46$, $T = 293(2)$ K, Wavelength: 0.71073 Å; Crystal system, Monoclinic, Space group: C_2/c; Unit cell dimensions: $a = 13.2300(17)$ Å, $b = 7.8740(17)$ Å, $c = 20.640(4)$ Å, $\beta = 104.571(4)°$; Volume: 2081.0(6) Å^3 $Z = 6$, Calculated density = 1.393 Mg m^{-3}, Absorption coefficient = 0.101 mm^{-1}, $F(000) = 920$; Theta range for data collection: 3.04–28.32°; Limiting indices = $-17 \leqslant h \leqslant 17$, $-10 \leqslant k \leqslant 5$, $-27 \leqslant l \leqslant 26$; Reflections collected/unique = 6673/2575 [$R_{(\mathrm{int})} = 0.0361$]; Completeness to theta = 28.32; 98.90%; Refinement method: Full-matrix least-squares on F^2, Goodness-of-fit on F^2: 1.042, Final R indices [$I > 2\sigma(I)$] = $R_1 = 0.0453$, $wR_2 = 0.1211$, R indices (all data): $R_1 = 0.0510$, $wR_2 = 0.1255$, Largest diff. peak and hole: 0.406 and -0.222 e Å^{-3}.