ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Nickel(II) complexes of 3-((E)-(6-ethoxybenzo[d]thiazol-2-ylimino)methyl)-4H-chromen-4-one: Synthesis and Physicochemical Characterization.

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ABSTRACT

A novel Schiff base ligand 3-((E)-(6-ethoxybenzo[d]thiazol-2-ylimino)methyl)-4H-chromen-4-one (EBTFC) derived from the 1:1 condensation of 2-amino 6-ethoxy benzothiazole and 3-formylchromone have been synthesized and characterized by CHNS analysis, IR, UV-Vis., ^{1}H NMR and ^{13}C NMR spectroscopic studies. A series of Ni(II) complexes, viz., $[Ni(EBTFC)_2]Cl_2$ (**1**), $[Ni(EBTFC)_2]Br_2$ (**2**), $[Ni(EBTFC)_2]I_2$ (**3**), $[Ni(EBTFC)_2](NO_3)_2$(**4**) and $[Ni(EBTFC)_2](ClO_4)_2$ (**5**) of the Schiff base ligand have been synthesized and characterized by elemental analysis, molar conductivity in non-aqueous solvents, CHNS analysis, spectroscopic studies and magnetic susceptibility measurements. The studies reveal that EBTFC acts as a neutral tridentate ligand coordinating through azomethine nitrogen, carbonyl oxygen and benzothiazole ring sulphur thus suggesting an octahedral geometry around the central metal ion in all the complexes.

Keywords: Schiff base, 3-formylchromone, 2-amino 6-ethoxy benzothiazole, Ni(II) complexes.

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INTRODUCTION

Coordination compounds exhibit different characteristic properties which depend on metal ion to which the ligands are bound, the nature of the metals as well as the type of ligand. Among coordination compounds, Schiff bases possess excellent properties such as, structural similarities with natural biological substances, simple procedures of preparation, flexibility in synthesis, wide range of applications and diverse structural modifications [1, 2]. Schiff bases are regarded as “privileged ligands” due to their ability to form complexes with a wide range of transition metal ions yielding stable and strongly coloured metal complexes. They are considered to be among the most important stereochemical models in transition metal coordination chemistry due to their preparative accessibility and structural diversity [3]. Their transition metal complexes have found application in various fields of human interest and continue to be of interest even after hundred years of study.

Considerable attention continues to be given to Schiff base ligands and their metal complexes since their properties can be greatly modified through the introduction of different substituents. Transition metal complexeshaving unique electronic and spectroscopic signatures offer a multitude of coordination geometries and mechanism of cytotoxic action which is related to DNA binding affinity [4].Designing of suitable polydentate Schiff base ligands to combine with a metal ion along with a pseudohalide anion has opened a new era of synthesizing metal complexes of particular choice [5]. So with the intention of obtaining information about the coordination chemistry of the metal complexes, it is proposed to study the novel Schiff baseligand3-((E)-(6-ethoxybenzo[d] thiazol-2-ylimino)methyl)-4H-chromen-4-one(EBTFC) and its Ni(II) complexes. Thenovel Schiff base has been characterized by TLC, elemental analysis, IR, UV-VIS, ^{1}H as well as ^{13}C NMR spectra. The new complexes have been characterized by several techniques such as elemental analysis, molar conductance in non-aqueous solvents, infrared as well as electronic spectraand magnetic susceptibility measurements.

EXPERIMENTAL

Reagents and equipment

High purity 2-amino 6-ethoxy benzothiazole (>99%) and 3-formylchromone (>98%) were purchased from Sigma Aldrich Chemical Co. USA. Nickel(II) chloride and nickel(II) nitrate were LR grade (E. Merck, India) and used as such. Nickel(II) bromide, iodide and perchlorate salts were prepared from Analar BDH nickel carbonate and the respective 50% acids by filtration, concentration and crystallization of the salts on a steam bath. All other chemicals and solvents were AR grade and used as such.

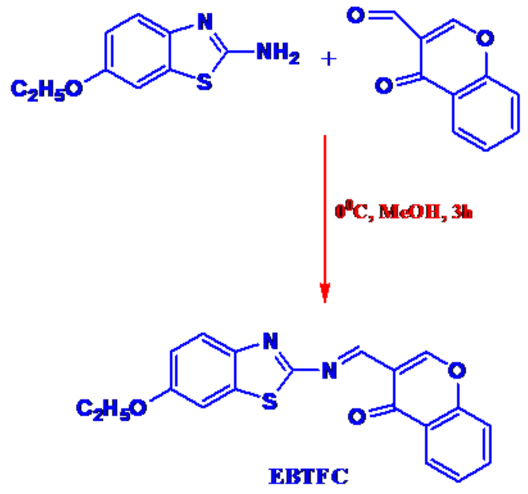
A Perkin–Elmer 240 CHN elemental analyzer was used to determine the carbon, hydrogen and nitrogen content in the synthesized compounds. All the complexes were analyzed for their metal, halide and perchlorate contents by standard methods. Molar conductivities were measured using freshly prepared 10^{-3}M solutions in acetonitrile, dimethylformamide and nitrobenzene at room temperature using a Toshniwal conductivity bridge with a dip-type conductance cell (cell constant 0.9835) which was calibrated with 0.01M KCl solution. The infrared spectra of the ligand and the complexes were recorded in the range 4000–400 cm^{-1} on a Shimadzu IR470 spectrophotometer and in the range 400–200 cm^{-1} on a Perkin–Elmer FTIR-8400S spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrophotometer using CD_3OD as solvent. Solid state electronic spectra in the range 1100–200nm were recorded using a UV–Vis 2450 spectrophotometer and in the range 1100–1500 nm on a Cary 2390 UV–Vis–NIR spectrophotometer. Magnetic susceptibility measurements were performed on pulverized samples at room temperature on a Sherwood Magway MSB Mk1balance. The diamagnetic corrections were calculated using Pascal’s constants.

Preparation and characterisation of the Schiff base ligand

3-((E)-(6-ethoxybenzo[d]thiazol-2-ylimino)methyl)-4H-chromen-4-one **(EBTFC)**

The ligand was prepared by stirring an ice-cold mixture of 2-amino 6-ethoxy benzothiazoleand 3-formylchromone in methanol medium for about 3h in 1:1 molar ratio (Scheme 1). The yellow precipitate obtained was filtered off, washed repeatedly with ice cold methanol, recrystallized from ethyl acetate and dried over phosphorus(V)oxide under vacuum. Yield: 85%.Anal. Calc. for $C_{19}H_{14}N_2O_3S$ (350.39): C, 65.13; H, 4.03; N, 7.99; S, 9.15.Found: C,65.30; H, 4.05; N, 8.12; S, 9.22%; IR (cm^{-1}): 1650 [ν(C=O)]; 1589 [ν(C=N)]; UV–Vis: (λ_{max}/nm): 387 (n–π*) and 267 (π–π*).^{1}H NMR (δ): 7.58 (sh s, 1H,-N=CH-), 3.98 (sh q, 2H, -CH_2-), 1.30 (sh t, 3H, -CH_3).

Scheme :1 Synthetic route for the preparation of the ligand EBTFC



EBTFC

Synthesis of metal complexes

1mmol of respective methanolic metal salt solution (10mL) was added drop wise to the boiling solution of EBTFC (2.2mmol) in dichloromethane (100mL). The mixture was refluxed for about 5h on a water bath and then concentrated. To the resulting solution diethyl ether was added and stirred well. The precipitate so obtained was filtered and washed repeatedly with hot methanol to remove any excess ligand. It was then recrystallized from ethanol and the solid obtained was dried under vacuum and kept over phosphorus(V)oxide.

[Ni(EBTFC)$_2$]Cl$_2$(1)

Yield: 79%. Anal. Calc. for $C_{38}H_{28}Cl_2N_4NiO_6S_2$(830.38): C, 54.96; H, 3.40; Cl, 8.54; N, 6.75; Ni, 7.07; S, 7.72%. Found: C, 54.82; H, 3.65; Cl, 8.47;N, 6.87; Ni, 7.32; S, 7.88%.

[Ni(EBTFC)$_2$]Br$_2$(2)

Yield: 75%.Anal. Calc. for $C_{38}H_{28}Br_2N_4NiO_6S_2$ (919.28): C, 49.65; H, 3.07; Br, 17.38; N, 6.09; Ni, 6.38; S, 6.98%. Found: C, 49.23; H,3.50; Br, 17.16; N, 6.02; Ni, 6.32; S, 7.05%.

[Ni(EBTFC)$_2$]I$_2$(3)

Yield: 72%.Anal. Calc. for $C_{38}H_{28}I_2N_4NiO_6S_2$ (1013.28): C, 45.04; H, 2.79; I, 25.05; N, 5.53; Ni, 5.79; S, 6.33%. Found: C, 45.25; H,3.05; I, 25.52; N, 5.91; Ni, 5.32; S, 6.21%.

[Ni(EBTFC)$_2$](NO$_3$)$_2$(4)

Yield: 76%.Anal. Calc. for $C_{38}H_{28}N_6NiO_{12}S_2$ (883.49): C, 51.66; H, 3.19; N, 9.51; Ni, 6.64; S, 7.26. Found: C, 52.31; H, 3.57; N, 9.14; Ni, 6.72; S, 7.66%.

[Ni(EBTFC)$_2$](ClO$_4$)$_2$(5)

Yield: 73%. Anal. Calc. for $C_{38}H_{28}Cl_2N_4NiO_{14}S_2$ (958.38): C, 47.62; H, 2.94; Cl, 7.40; N, 5.85; Ni, 6.12; S, 6.69%. Found: C, 48.26; H, 3.15; Cl, 7.32;N, 6.08; Ni, 6.32; S, 6.89%.

Caution! Perchlorate complexes are potentially explosive. They should not be prepared and stored in large amounts.

RESULTS AND DISCUSSION

General properties

The ligand and the complexes are stable at room temperature and are non-hygroscopic solids with brown colour. The complexes are soluble in common organic solvents like acetone, acetonitrile, dimethylformaide, ethanol and methanol but insoluble in benzene, chloroform, ethyl acetate and toluene. Micro analytical and molar conductance data of the complexes are given in table 1. The analytical data of the complexes agree very well with the general formulae $Ni(EBTFC)_2X_2$ where X = Cl^-, Br^-, I^-, NO_3^- or ClO_4^-.The molar conductance values of the complexes (10^{-3}M solutions) in the non-aqueous solvents acetonitrile, DMF and nitrobenzene indicate a 1:2 electrolytic behavior for all the complexes [6]. Thus the complexes may be formulated as $[Ni(EBTFC)_2]X_2$ (where X = Cl^-, Br^-, I^-, NO_3^- or ClO_4^-).

Infrared Spectra

The IR spectra of the complexes were compared with that of the Schiff base inorder to determine the coordination sites involved in chelation (table 2).EBTFC exhibits a strong band at 1650cm^{-1} corresponding to the stretching vibrations of the chromone ring carbonyl oxygen. The C=O band is shifted to the lower frequency region of 1640-1644cm^{-1} indicating the coordination of carbonyl oxygen in all the complexes [7]. An intense band observed at 1589cm^{-1}attributable to the C=N stretch in EBTFC is shifted to the region 1573-1581cm^{-1} in the complexes suggesting the coordination of azomethine nitrogen [8]. The characteristic absorption at 749cm^{-1} in the ligand is assigned to the C-S-C stretching of benzothiazole moiety of EBTFC [9]. This band is found to shift to 733-729cm^{-1} indicating the coordination through benzothiazole ring sulphur. Thus EBTFC acts as a neutral tridentate ligand coordinating through the azomethine nitrogen, carbonyl oxygen and benzothiazole ring sulphur. The new bands in the spectra of complexes at about 554-562 and 440-461cm^{-1} assigned to $\nu_{(Ni-O)}$ and $\nu_{(Ni-N)}$ stretching vibrations respectively, are conclusive evidence of coordination of the metal ion by the ligand [10].

The nitrate complex exhibits vibrational frequencies characteristic of uncoordinated nitrate ions. A very strong band observed at 1384cm^{-1} is due to the ν_3 vibration of the nitrate ion of D_{3h} symmetry indicating the presence of uncoordinated nitrate ion in the complex [11]. This is supported by another band of medium intensity at 829cm^{-1}, which is attributed to the ν_2 vibrations of the nitrate (D_{3h}) ion [11].

In the perchlorate complex,the very strong band observed at 1087cm^{-1} is attributable to the ν_3 vibration of uncoordinated perchlorate ion of T_d symmetry [12]. The band at 624cm^{-1} due to ν_4 vibration (T_d) again supports the existence of uncoordinated perchlorate ion in the complex.

The absence of the bands due to $\nu_{(Ni-X)}$ stretching in the far IR spectra of complexes (**1**), (**2**) and (**3**) suggests that the chloride, bromide and iodide ions remain uncoordinated to the metal ion.The above results along with the conductance data indicate that all of the chloride, bromide, iodide, nitrate and perchlorate ions are uncoordinated to the metal ion and remain as counter anions outside the coordination sphere.

Electronic Spectra and Magnetism

The electronic spectrum of EBTFC exhibits two main peaks at 387 and 267nm which are assignable to the n-π* and π-π* transitions respectively [13]. In all the complexes, the n-π* and π-π* bands are blue shifted to 335-342nm and 234-241nm respectively (table 3). The complexes also show an intense absorption in the 390-405nm region which may be due to charge transfer transition.All the complexes show three characteristic bands in the regions 1038-1068nm, 618-685nm and 476-500nm corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ thus suggesting an octahedral geometry around Ni(II) ion [14].The room temperature magnetic moments of Ni(II) complexes (**1**)-(**5**) were in the range 2.80-2.96 BM (table 3) suggesting an octahedral configuration around the Ni(II) ion [15].

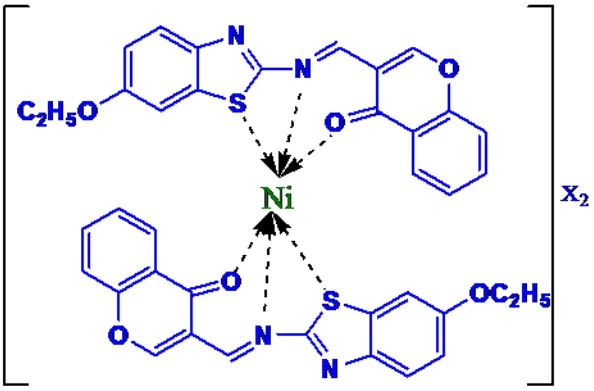
^{1}H and ^{13}C NMR Spectra

The ^{1}H NMR spectrum of EBTFC shows a triplet at 1.30δ which is assigned to the $-CH_3$ protons and a quartetaround3.98 δ due to $-CH_2-$ protons. Further, the sharp singlet at 7.58 δ is assigned to the azomethine proton in EBTFC.

The ^{13}C NMR spectrum of EBTFC shows the presence of one keto, one azomethine, one ethyl and eleven aromatic signals for a total of 19 carbon atoms.Thesinglet peaks at 188.34 and 153.58δ are attributed to the keto and azomethine carbon atoms respectively. The singlet signal at 174.88 δ is due to the carbon atom in the –S-C=N moiety of benzothiazole. The eleven down field signals from 106.20-163.42 δ show the presence of aromatic carbon atoms. The signalsin the range63.65-63.53δ and 14.71-14.61 δ is attributed to ethyl carbon atoms.The above results confirm the proposed structure of the ligand. Owing to their paramagnetic nature, the ^{1}H NMR and ^{13}C NMR spectra of the complexes could not be studied.

Based on the above observations the following tentative structures (figure 1) may be assigned to the complexes.

Figure 1 Tentative structures of the Ni(II) complexes of EBTFC



$(X = Cl^-, Br^-, I^-, NO_3^- \text{ or } ClO_4^-)$

CONCLUSION

A novel Schiff base ligand 3-((E)-(6-ethoxybenzo[d]thiazol-2-ylimino)methyl)-4H-chromen-4-one (EBTFC) has been synthesized and characterized. Also a series of its mononuclear nickel(II) complexes $[Ni(EBTFC)_2]Cl_2$ (**1**),$[Ni(EBTFC)_2]Br_2$(**2**), $[Ni(EBTFC)_2]I_2$ (**3**), $[Ni(EBTFC)_2](NO_3)_2$(**4**) and $[Ni(EBTFC)_2](ClO_4)_2$ (**5**) were preparedand characterized.The infrared spectra reveal that in all the complexes EBTFC acts as a neutral tridentate ligand coordinating through azomethine nitrogen, carbonyl oxygen and benzothiazole ring sulphur. The molar conductance data and infrared spectra indicat e non-coordination of anions and thus all the anions exist as counter ions in the complexes. The electronic spectra and magnetic moment data suggest an octahedral geometry around the central metal ion in all the complexes.

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