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ORIGINAL ARTICLE

Synthesis, spectral, thermal, potentiometric and antimicrobial studies of transition metal complexes of tridentate ligand

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Abstract A series of metal complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) have been synthesized with newly synthesized biologically active tridentate ligand. The ligand was synthesized by condensation of dehydroacetic acid (3-acetyl-6-methyl-(2*H*) pyran-2,4(3*H*)-dione or DHA), *o*-phenylene diamine and fluoro benzaldehyde and characterized by elemental analysis, molar conductivity, magnetic susceptibility, thermal analysis, X-ray diffraction, IR, ^{1}H-NMR, UV–Vis spectroscopy and mass spectra. From the analytical data, the stoichiometry of the complexes was found to be 1:2 (metal:ligand) with octahedral geometry. The molar conductance values suggest the non-electrolyte nature of metal complexes. The IR spectral data suggest that the ligand behaves as a dibasic tridentate ligand with ONN donor atoms sequence towards central metal ion. Thermal behaviour (TG/DTA) and kinetic parameters calculated by the Coats–Redfern and Horowitz–Metzger method suggest more ordered activated state in complex formation. To investigate the

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relationship between stability constants of metal complexes and antimicrobial activity, the dissociation constants of Schiff bases and stability constants of their binary metal complexes have been determined potentiometrically in THF–water (60:40%) solution at 25 ± 1 °C and at 0.1 M $NaClO_4$ ionic strength. The potentiometric study suggests 1:1 and 1:2 complexation. Antibacterial and antifungal activities *in vitro* were performed against *Staphylococcus aureus*, *Escherichia coli* and *Aspergillus niger*, *Trichoderma*, respectively. The stability constants of the metal complexes were calculated by the Irving–Rosotti method. A relation between the stability constant and antimicrobial activity of complexes has been discussed. It is observed that the activity enhances upon complexation and the order of antifungal activity is in accordance with stability order of metal ions.

1. Introduction

The Schiff base ligands and their metal complexes find applications in the fields of food and dyes industry, agriculture, analytical chemistry, catalysis, polymer sciences, biological science as antimicrobial agents, medical science as anticancer, antiseptic, antidiarrhoeal, antiulcer agents, in liquid crystal devices (LCD), metal corrosion inhibition and as myocardial perfusion imaging agents (Koubek et al., 1966). These compounds are regarded as the model system of biochemical interest (Dey, 1974). Various studies have shown that, the azomethine group (>C═N–) in Schiff base metal complexes has considerable biological significance and found to be responsible for biological activity such as fungicidal and insecticidal (Popp, 1961). Schiff bases of amino guanidine and aromatic aldehydes were studied for their antiviral, tuberculostatic and antipoliovirus activities (Mane et al., 2001).

The structural and interesting biological properties of DHA appeal to inorganic chemists working in the field of coordination chemistry. Schiff bases and their metal complexes exhibit a wide range of biological activities and various structural features. In view of the enormous importance of DHA and its metal complexes it is thought worthwhile to synthesize the Schiff base of DHA and its metal complexes. One of the oxygen heterocyclic compounds 3-acetyl-6-methyl-2*H*-pyran 2,4(3*H*)-dione (DHA) was reported to be an excellent chelating agent and possesses promising fungicidal, bactericidal, herbicidal and insecticidal activities (Suryarao et al., 1978, 1980; Schleiffenbaum et al., 1992; Stanley et al., 1996). It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems (Levai and Jeko, 2006).

The structural and interesting biological properties of DHA appeal to inorganic chemists working in the field of coordination chemistry. In view of the enormous importance of DHA and its metal complexes it is thought worthwhile to synthesise the Schiff bases of DHA and their metal complexes. Literature survey reveals that little attention has been given on tridentate Schiff bases of DHA containing ONN donor systems. In continuation of our earlier work (Munde et al.,2009, 2010;Halpern et al., 1971; Shirodkar et al., 2001), we have prepared tridentate Schiff base and its metal complexes, whose structure agrees with the above mentioned structural and coordinative patterns for biological activity. The solid complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) with this ligand have been prepared and characterized by different physicochemical methods. Stability constants of these complexes are also determined potentiometrically. The structure-activity correlation of Schiff base and its metal complexes is discussed on the basis of their stability constants.

2. Experimental

o-Phenylenediamine and benzaldehyde AR grade were used for synthesis of ligand. DHA (Purity ⩾ 99%) was purchased from E. Merk and used as supplied. AR grade metal nitrates were used for complex preparation. AR grade solvents were used for spectral measurements. The carbon, hydrogen and nitrogen contents were determined on Perkin–Elmer (2400) CHNS analyzer. IR spectra in the range of 4000–400 cm^{-1} were recorded on Jasco FT-IR-4100 spectrometer using KBr pellets. ^{1}H-NMR spectra of the ligand was recorded in $CDCl_3$ using TMS as an internal standard. The TG/DTA and XRD were recorded on Perkin–Elmer TA/SDT-2960 and Philips 3701, respectively. The UV–Vis spectra of the complexes were recorded on JascoUV-530 Spectrophotometer. Magnetic susceptibility measurements of the metal complexes were done on a Guoy balance at room temperature using Hg.[$Co(SCN)_4$] as calibrant. Molar conductance of complexes was measured on Elico CM-180 conductometer using 1 mM solution in dimethyl sulphoxide. Elico digital pH metre (model Li-127) equipped with a CL-51B combined electrode was used for pH measurements. The pH metre was calibrated against standard buffers (pH 4.02 and 9.18) before measurements. pH metre readings were corrected for organic-aqueous media. Titrations were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of 0.1 M ($NaClO_4$). The solutions were titrated pH metrically against (0.2 N) NaOH.

2.1. General procedure for the synthesis of ligand

2.1.1. Step I

The ligand was prepared by modification of reported method (Jha and Joshi, 1984; Qayyoom et al., 1982) In a 50 mL solution of 0.001 mol (0.168 g) of DHA, 0.001 mol (0.108 g) of *o*-phenylenediamine was refluxed in super dry ethanol for about 3 h. Then it was cooled to room temperature. On cooling, the solid white colored intermediate compound, mono-Schiff base was obtained with 80% yield.

2.1.2. Step II

0.001 mol of intermediate (0.258 g) was then refluxed with 0.001 mol (0.10 mL) of fluoro benzaldehyde (0.107 mL) in super dry ethanol for 6 h. The precipitate thus formed was filtered, dried in vacuum over $CaCl_2$ and recrystallised in ethanol (yield: 73%).