J. Indian Chem. Soc.,
Vol. 91, September 2014, pp. 1-9

Microwave assisted synthesis, spectroscopic characterization and luminescence property of transition metal complexes of 2-(3-phthalylhydrazidylazo)-ethylacetoacetate

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Manuscript received online 06 November 2013, accepted 11 March 2014

Abstract : A simple, efficient and green synthetic protocol of bivalent transition metal complexes of a luminol derivative namely (3-phthalylhydrazidylazo)ethylacetoacetate under microwave irradiation in the absence of solvent has been described. The complexes have been characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility measurements and various spectral studies. The spectral studies have revealed that the ligand acts as monobasic tridentate coordinating to the metal ion through acetyl carbonyl, hydrazo nitrogen and amido carbonyl of phthalylhydrazide moiety. The electron paramagnetic resonance spectra of copper(II) complex has shown that the metal-ligand bond has considerable covalent character. The ligand and nickel(II) complex have been subjected to powder X-ray diffraction study. The high degree of crystallinity of the ligand has been lost on complexation with metal ion. The electrochemical behavior of the copper(II) complex has been also examined. The luminescence properties of complexes have been compared with that of the free ligand.

Keywords : Microwave assisted synthesis, ethylacetoacetate, phthalylhydrazide, XRD, electrochemical behavior, luminescence.

Introduction

Luminol and its derivatives have been extensively used as chemiluminescent reagents. The chemiluminescence of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) was first described by Albrecht[1]. Since then, luminol and its derivatives have been extensively studied and applied for several analytical applications[2–6]. Electrogenerated chemiluminescence is of growing importance in many areas of analytical interest. It can offer a number of advantages for the detection of a wide range of analyte[7]. Recently, chemiluminescence has been an attractive detection method for HPLC. With chemiluminescence detection, luminol related compounds have been widely utilized as chemiluminescence derivatization reagents, because of their high sensitivity and selectivity. However metal complexes of luminol and its derivatives have received only sporadic attention so far when compared to its analytical applications, presumably due to the poor solubility of luminol and its derivatives in common organic solvents used for synthetic purposes. From a safety and environmental point of view, the synthetic protocol is saddled with a serious drawback, especially when the reactants are insoluble in common solvents used for the synthetic purposes. In the present work it has been overcome by microwave assisted solvent free synthesis. This new synthetic approach has got several advantages over the conventional method[8]. In this investigation luminol has been incorporated into a β-ketoester through azo coupling. Apart from the synthetic aspects, the structural diversities exhibited by arylazo derivatives of β-diketones and their metal complexes have evolved considerable interest. The structure of such coupling products, capable of existing in different tautomeric forms, has generated so much arguments and speculations as hardly any other topic in the whole realm of organic chemistry done so far[9,10]. Although several metal complexes of carbocyclic azo derivatives have been extensively investigated, those derived from heterocyclic systems have received comparatively less attention[11]. The present work deals with the synthesis and spectroscopic characterization of some complexes of some transition