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ORIGINAL ARTICLE

Pd(II) complexes bearing chromone based Schiff bases: Synthesis, characterisation and biological activity studies

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KEYWORDS

Antioxidant;
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Formyl chromone;
Palladium(II)

Abstract Pd(II) complexes of 3-formyl chromone Schiff bases such as 3-((2-hydroxyphenylimino) methyl)-4H-chromen-4-one (HL_1), 2-((4-oxo-4H-chromen-3-yl)methylneamino)benzoic acid (HL_2), 3-((3-hydroxypyridin-2-ylimino)methyl)-4H-chromen-4-one (HL_3), 3-((2-mercaptophenylimino) methyl)-4H-chromen-4-one (HL_4) and 3-((pyridine-2-ylimino)methyl)-4H-chromen-4-one (L_5) have been synthesised and characterised by elemental analysis, molar conductivity, IR, electronic, magnetic, TG–DTA, powder XRD and fluorescence spectral data. From the analytical, electronic and magnetic data square-planar geometry has been proposed for all the Pd(II) complexes. Powder XRD studies indicate the crystalline state of the Pd(II) complexes. The antimicrobial activity of Pd(II) complexes was performed against two Gram(−ve), two Gram(+ve) and fungal microorganisms and the results indicate that, complexes show better microbial inhibition activity than the ligands. Pd(II) complex of HL_1 displayed comparable antioxidant activity with reference to the standard drug (BHT). Agarose gel electrophoresis assay demonstrates the ability of complexes to cleave the pUC19 plasmid DNA. The cytotoxicity was tested by the MTT assay. The results indicate that the complexes exert cytotoxic effects against tested cell lines but their cytotoxicity is less than that of cisplatin.

1. Introduction

Formyl chromone Schiff bases have been the centre of attraction for many workers in the current research due to their miscellaneous activities. Chromones are naturally occurring compounds which are able to cause cytotoxic effect in various types of cells. They are widely known to have anticancer, antioxidant, antiproliferative, antiHIV, antiinflammatory, and many other activities (Martens and Mithofer, 2005; Di Braccio et al., 2003; Middleton et al., 2000). Since the last decade, me-

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tal coordination chemistry has been one of the most efficient strategies in the design of drugs (Jones and Thornbak, 2007). Many literature reports revealed that chromone and its derivatives are able to form stable and coloured complexes with various metal ions (Anitha et al., 2012; Li and Yang, 2010). According to literature reports, metal complexes of the chromone moiety possess various biological activities in some cases comparable with cisplatin (which is an effective anticancer drug) (Grazul and Budzisz, 2009) and some metal complexes which are connected with reactions generating free radicals, may in some cases obtain additional antioxidant ability (Kostyuk et al., 2001; Grazul et al., 2012). These metal complexes are also used in various fields (Nijhawan and Kakkar, 1998).

A large number of platinum and palladium complexes containing amine based ligands have become the subject of intensive research, since they are structurally related to cisplatin. The success of cisplatin and other Pt(II) complexes in the treatment of ovarian, testicular, neck and head, oesophageal and non-small cell lung cancers (Todd and Lippard, 2009; Eastman, 1999; Montana and Batalla, 2009; Abu-Surrah and Kettunen, 2006; akomska, 2009) and similar properties of Pt(II) and its congener Pd(II), have led to a large effort in the search to find Pd(II) antitumour drugs that are effective against Pt(II) resistant therapies and that have fewer side effects (Garoufis et al., 2009; Abu-Surrah et al., 2008; Gao et al., 2009; Štarha et al., 2009). The main target of chemotherapy is the destruction of tumour cells without any undue influence on proper cells. Compared to palladium and platinum complexes, palladium complexes are hydrolyzed 10^5 times faster than their corresponding platinum analogues, which could lead to the hydrolysis of Pd(II) complexes before they reach their target DNA (Polyanskaya et al., 2010). Pd(II) complexes also posses antimicrobial and antioxidant activity etc. (Spera et al., 2011; Ramachandran et al., 2012). This has provoked interest in the design of Pd(II) complexes.

As part of our on-going research work on the synthesis of metal complexes with Schiff bases derived from formyl chromone and aromatic amines i.e. 3-((2hydroxyphenylimino) methyl)-4H-chromen-4-one (HL_1), 2-((4-oxo-4H-chromen-3-yl)methylneamino)benzoic acid (HL_2), 3-((3-hydroxypyridin-2-ylimino)methyl)-4H-chromen-4-one (HL_3), 3-((2-mercaptophenylimino) methyl)-4H-chromen-4-one (HL_4) and 3-((pyridine-2-ylimino)methyl)-4H-chromen-4-one (L_5) (Kavitha and Laxma Reddy, 2016; Kavitha et al., 2013a,b), we present here the preparation, characterisation and evolution of biological activities (antimicrobial, antioxidant, cytotoxicity and DNA cleavage) of Pd(II) complexes with the 3-formyl chromone Schiff base ligands (HL_1, HL_2, HL_3, HL_4 and L_5).

2. Experimental

2.1. Reagents and equipments

All chemicals and solvents used were of AR grade. Palladium dichloride was obtained from Jhonson Matthew Chemicals (England).

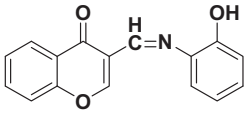
The UV–Vis spectra of the ligands and their metal complexes were recorded on an Analytikzena Specord 205 UV–Vis spectrophotometer. Molar conductance of the complexes was measured in DMF at 1×10^{-3} M using a Digisun conductivity meter. Elemental analysis (C, H, and N) was performed using Perkin Elmer CHN analyser. The chloride ion was estimated by the Volhard's method (Vogel, 1961). The IR pectra (4000–400 cm^{-1}) in KBr discs were recorded on TENSOR 2 spectrophotometer. Thermal studies of the complexes were carried out on a Perkin Elmer diamond TGA instrument at a heating rate of 10 °C and a nitrogen flow rate of 20 mL/min. The magnetic susceptibilities of Pd(II) complexes were measured with a Sherwood scientific balance. Fluorescence spectra were recorded using Perkin Elmer LS 55 fluorescence spectrometer. The X-ray powder diffraction analysis was carried out by using Xpert-Pro X-ray diffractometer using Cu-Kα (1.5360 Å) radiation.

2.2. Synthesis of ligands

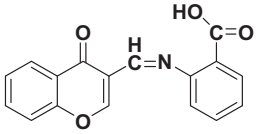
Schiff base ligands HL_1, HL_2, HL_3, HL_4 and L_5 (Fig. 1) were synthesised and characterised according to the literature (Sigg et al., 1982; Khan et al., 2010; Kavitha et al., 2012, 2013b; Kavitha and Laxma Reddy, 2016).

2.3. Synthesis of Pd(II) complexes

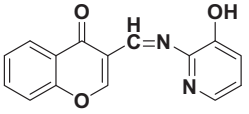
All the palladium(II) complexes were prepared using the general procedure as given below. $PdCl_2$ solution in 0.1 M HCl



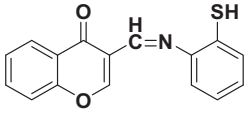
3-(-(2-hydroxyphenylimino)methyl)-4*H*-chromen-4-one
(HL_1)



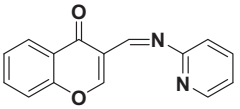
2-((4-oxo-4*H*-chromen-3-yl)methyleneamino)benzoic acid
(HL_2)



3-((3-hydroxypyridin-2-ylimino)methyl)-4*H*-chromen-4-one
(HL_3)



3-(-(2-mercaptophenylimino)methyl)-4*H*-chromen-4-one
(HL_4)



3-((pyridin-2-ylimino)methyl)-4*H*-chromen-4-one
(L_5)

Figure 1 Structures of ligands.