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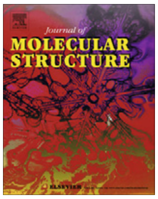

Synthesis and X-ray structural studies of Cd(II) and Ni(II) complexes of 5-(4-methoxy phenyl), 5-(2-pyridyl) and 5-(2-methoxy phenyl)-1,3,4-oxadiazole-2-thione

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ABSTRACT

Three new mixed ligand complexes [Cd(en)$_2$(4-mpot)$_2$] (**1**) [Ni(2-pytone)$_2$(en)$_2$] (**2**) and [Ni(2-mpot)$_2$(en)$_2$] (**3**) {4-mpot = 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thione, 2-pytone = 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione, 2-mpot = 5-(2-methoxy-phenyl)-1,3,4-oxadiazole-2-thione} have been prepared containing en as co-ligand. Potassium N-(4-methoxy benzoyl)-hydrazinecarbodithioate cyclized to 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thiol on addition of tetrabutylammonium bromide which then reacted with Cd(OAc)$_2$·2H$_2$O and ethylenediamine to form complex **1**, whereas potassium N-(2-methoxy benzoyl/pyridine-2-carbonyl)-hydrazinecarbodithioates (RCONHNHCSSK) underwent cyclization during complexation in the presence of en to give the complexes of the corresponding 5-aryl-1,3,4-oxadiazole-2-thiones. The complexes have been characterized by physicochemical techniques and single crystal X-ray structure determination. In the complexes the metal center has a six coordinate octahedral arrangement coordinated by 4N atoms of two en and two covalently bonded N atoms of the oxadiazole-2-thione anions. All the complexes contain extended hydrogen bonding providing supramolecular framework.

1. Introduction

The coordination chemistry of nitrogen–sulfur chelating ligands is an emerging and rapidly developing area of research [1–3]. The multifaceted chemistry of metal sulfur bonds are apparent in the application of these compounds as catalyst in biological and non-biological processes [4,5]. A class of nitrogen sulfur ligand such as N-aroyl dithiocarbazates and their salts could be converted to 1,3,4-oxadiazole-2-thione, which are biologically important molecules [6–8]. The oxadiazole molecules act as spacer *via* coordination, hydrogen bonding and show intermolecular cooperative interaction [9]. 1,3,4-oxadiazole derivatives, which belong to an important group of heterocyclic compounds is the subject of extensive study in the recent years [7,8]. They show diverse biological activities, such as anti-tuberculostatic, anti-inflammatory, anti-fungal, analgesic, and anti-convulsant [10–12]. Although some work has been reported on the binary complexes of 5-phenyl-1,3,4-oxadiazole-2-thione [13], 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione [14–19] and 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione [20], but scanty of information is available on the mixed ligand complexes of these ligands. Since 1,3,4-oxadiazole-2-thiones may exist in both thione and thiol forms in solution [21,22], it will therefore be of interest to investigate the bonding mode of the ligand in the complexes. In view of this, we have prepared and characterized the Cd(II) complex of 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thione and Ni(II) complexes of 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione and 5-(2-methoxy-phenyl)-1,3,4-oxadiazole-2-thione in the presence of ethylenediamine which act as a co-ligand.

2. Experimental

2.1. Chemical and starting materials

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. Picolinic acid hydrazide (Sigma–Aldrich), CS$_2$ (S D Fine Chemicals, India) and KOH (Qualigens) were used as received. 2-Methoxy benzoic acid hydrazide and [Ni(en)$_2$(SCN)$_2$] were prepared by reported methods [23,24]. All the solvents were purchased from Merck and used after purification. The yield calculation is based on the weight of the ligand or the initial starting material where intermediate were not isolated.

2.2. Physical measurements

Carbon, hydrogen and nitrogen contents were estimated on a Carlo Erba 1108 model microanalyser. Magnetic susceptibility measurements were performed at room temperature on a Cahn

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Faraday balance using Hg[Co(NCS)$_4$] as the calibrant. Electronic spectra were recorded on a Shimadzu 1700 UV–Vis spectrophotometer as Nujol mulls. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100-FT IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d$_6$ and CDCl$_3$ on a JEOL AL 300 FT NMR spectrometer using TMS as internal reference.

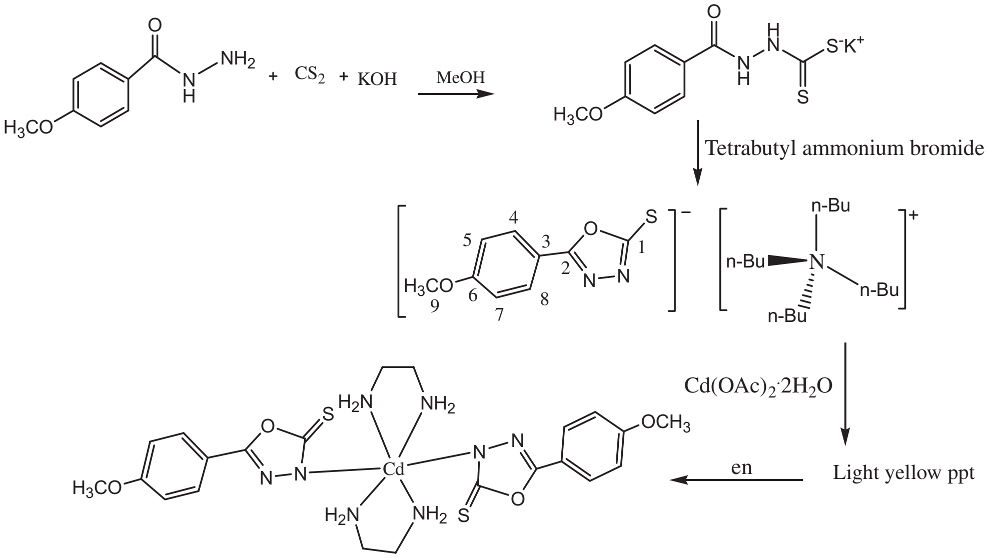
2.3. X-ray crystallography

Crystals suitable for X-ray analyses of the complexes **1**, **2** and **3** were grown at room temperature. Data for complexes **1**, **2** and **3** were recorded at 293(2) and 296(2) on an Oxford Diffraction Gemini [25] and a Bruker three-circle diffractometer, respectively equipped with a CrysAlis Pro./SMART 6000 CCD software using a graphite mono-chromated Mo Kα (λ = 0.71073 Å) radiation source. The structures were solved by direct methods and refined (SHELX-08) against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model [26]. The MERCURY package was used for molecular graphics [27]. Molecular structure diagrams were generated by use of the ORTEP-3 for windows program [28].

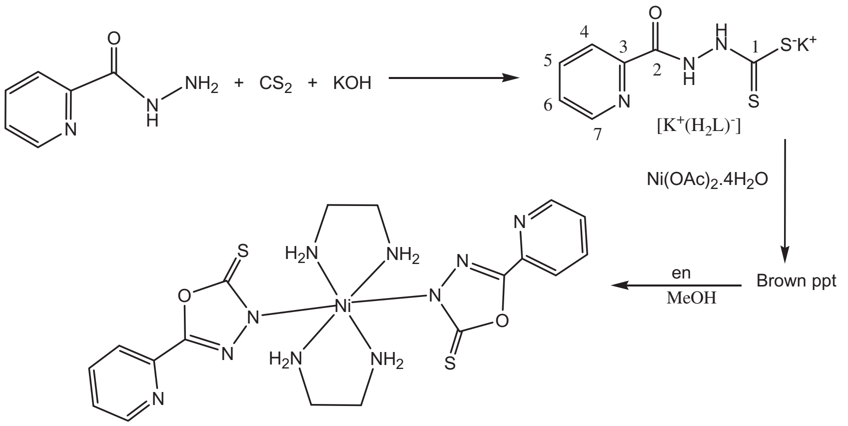
2.4. Synthesis

2.4.1. Synthesis of tetrabutylammonium 5-(4-methoxy phenyl)-1,3,4-oxadiazole-2-thiol

Tetrabutylammonium 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thiol was synthesized by adding CS$_2$ (1.5 mL, 20 mmol) dropwise to a suspension of 4-methoxy benzoic acid hydrazide (3.32 g, 20 mmol) in methanol (30 mL) in the presence of potassium hydroxide (1.2 g, 20 mmol) and stirring the reaction mixture for 30 min at room temperature. The yellow solid product obtained in the above reaction was dissolved in water and an aq. solution of tetrabutylammonium bromide (3.22 g, 10 mmol) was added. The resulting yellow solid was obtained which was filtered off and dried. Yield (1.625 g, 60 %). Anal. Found: C, 66.72; H, 9.55; N, 9.30; S, 7.05 %. Calc. for $C_{25}H_{43}N_3O_2S$ (449.69): C, 66.77; H, 9.63; N, 9.34; S, 7.13 %. M.p.105 °C; IR (KBr, ν, cm^{-1}): 1602s ν(C=N), 1066s ν(N—N), 988s ν(C=S). ^{1}H NMR (CDCl$_3$, TMS; δ, ppm): 10.8 (s, 1H, NH), 3.80 (s, 3H, OCH$_3$), 7.0–7.7 (m, 4H, C$_6$H$_5$), 1.0 (t, 3H, CH$_3$), 1.4 (sext, 2H, CH$_2$), 1.6 (quint., 2H, CH$_2$) 3.3 (t, 2H, N—CH$_2$). ^{13}C NMR (CDCl$_3$; δ, ppm): 197.15 (C—S), 160.38 (C=N), 113.92



Scheme 1. Synthesis of tetrabutylammonium 5-(4-methoxy phenyl)-1,3,4-oxadiazole-2-thiol and Cd(II) complex.



Scheme 2. Preparation of [Ni(2-pytone)$_2$(en)$_2$] (**1**).