Inorganica Chimica Acta 445 (2016) 70–78

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Regioselective Mannich bases of pyrrole-2-carbaldehyde and binuclear copper(II) complexes of bis(iminopyrrolyl) ligand containing the piperazine ring

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A R T I C L E I N F O

Article history:
Received 20 August 2015
Received in revised form 3 December 2015
Accepted 12 February 2016
Available online 21 February 2016

Keywords:
Copper(II)
Bis(iminopyrrolyl)
Mannich reaction
Regioselectivity
Schiff base
Hydrogen bonding

A B S T R A C T

Iminopyrrolyl ligands have attracted an attention in the field of coordination chemistry. As every iminopyrrolyl ligand contains at least one acidic pyrrole NH group, it often forms an anionic five-membered chelate ring with a metal. Unlike the familiar pincer framework ligand systems, iminopyrrolyl coordination chemistry is in a developing stage. Hence, we set the synthesis of bis(iminopyrrole) framework ligand containing the piperazine ring as a spacer unit between two mono(iminopyrrolyl) moieties. The Mannich reaction of pyrrole-2-carbaldehyde with piperazine and formaldehyde afforded two new dialdehydes: *N*,*N*′-bis(5-formylpyrrol-1-ylmethyl)piperazine **1** and *N*,*N*′-bis(5-formylpyrrol-2-ylmethyl)piperazine, **2**, which are regioselective products formed in good yields. The pyrrole N aminomethylated dialdehyde **1** was isolated in the absence of an added acid. Conversely, the pyrrole α-C aminomethylated dialdehyde compound **2** was obtained in the presence of a mineral acid. They have different spectroscopic and physical properties. Even they offered different Schiff bases under the same reaction conditions. The Schiff base condensation reaction of **2** with 2,6-diisopropylanilline in the presence of HNO_3 gave the expected [1+2] Schiff base in 53% yield after column separation. Conversely, the other dialdehyde **1** yielded the piperazinylmethyl C–N bonds hydrolyzed known 2-iminopyrrole compound. Further, the treatment of the structurally characterized [1+2] bis(iminopyrrolyl) ligand with copper(II) carboxylates $[Cu(OOCR)_2(H_2O)]$ (R = H, Me and Ph) gave three different binuclear five-coordinate copper(II) complexes. Their structures were determined by single crystal X-ray diffraction studies. Interestingly, the piperazine ring nitrogens are not coordinated, rather involved in intramolecular hydrogen bonding interactions with the coordinated solvent molecules at the copper atom.

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1. Introduction

The mono(iminopyrrolyl) and bis(iminopyrrolyl) ligand systems possess an attractive coordination motif with metals, which drives their metal complexes synthesis [1]. Iminopyrrolyl ligands are conveniently synthesized by condensation reactions of the corresponding pyrrole aldehyde with a variety of primary amines, which have led to a variety of iminopyrrolyl ligands having varying steric and electronic properties [2]. In addition, ligands containing two iminopyrrole moieties linked through some aromatic or aliphatic spacer unit have also been developed [3]. Iminopyrrolyl metal complexes have been used as catalysts for ethylene polymerization [4] and the ring opening polymerization of ε-caprolactone [5] reactions. Similarly, a large progress has been made on the analogous bis(imino)dipyrromethanes and their coordination chemistry [6]. In addition, one of the noticeable features of metal complexes containing pyrrole based ligands is the binding mode of the pyrrolidine ring; it coordinates primarily in two modes: κ^1N (terminal) and η^5/κ^1N (bridging), which facilitate multinuclear complex formation [7].

Gmeiner and co-workers have reported the regioselective formylation of the piperazinylmethyl substituted pyrrole [8]. Keypour et al. have reported several Schiff bases containing the piperazine ring and studied their coordination chemistry [9]. In addition, Lee, Huang and co-workers have recently reported the mono- and dipiperazinylmethyl substituted pyrrole by the Mannich reactions of pyrrole [10]. We are interested in developing metal complexes of pyrrole-based ligand systems and their catalytic applications. Recently, we reported a few palladium complexes containing bis(iminopyrrolylmethyl)amine ligand, which shows an interesting amine–azafulvene tautomeric structure upon

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http://dx.doi.org/10.1016/j.ica.2016.02.023
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complex formation, and their Suzuki cross coupling reactions [11]. These interesting properties of iminopyrrolyl ligands have made us to become interested in designing different iminopyrrolyl ligands for metal complexes study. Herein, we report two new regioselectively formed dialdehydes containing the piperazine ring as a spacer unit via the Mannich reaction of pyrrole-2-carbaldehyde. In addition, we also report synthesis and structural characterization of binuclear copper(II) complexes containing a new bis (iminopyrrolyl) ligand derived from the dialdehyde molecule.

2. Results and discussion

2.1. Synthesis and characterization of dialdehydes

Pyrrole-2-carbaldehyde reacts with a mixture of piperazine and formaldehyde in 2:1:2 molar ratios, respectively, to give the pyrrole N aminomethylated dialdehyde compound **1**, which was isolated as a colorless solid from the reaction mixture without further purification in 71% yield. Interestingly, when the same reaction was carried out in the presence of an acid, the pyrrole α-C aminomethylated dialdehyde compound **2** was obtained in almost the same yield as **1** (Scheme 1). Although the HRMS spectra of **1** and **2** showed the same molecular ion peak at *m*/*z* 301.1626 (calc. mass 301.1665) corresponding to their [M+H$^+$] ions, these regioselectively formed products could be differentiated by NMR and IR methods. In the ^{1}H NMR spectrum of **1** in $CDCl_3$, the pyrrole ring CH resonances appeared as two multiplets at $\delta = 6.95$ and 6.23 ppm with their integrated intensity ratio of 2:1. In contrast, compound **2** showed the 1:1 integrated intensity ratio for the pyrrole ring CH protons which appeared as multiplets at $\delta = 6.89$ and 6.16 ppm; its pyrrolic NH resonance appeared as broad singlet at $\delta = 9.61$ ppm. Further, the N-bound methylene groups in **1** resonates as a sharp singlet at $\delta = 5.15$ ppm, which is shifted downfield by 1.59 ppm as compared to the resonance of the same group in **2** appearing at $\delta = 3.56$ ppm. Furthermore, this regioselectivity is supported by DEPT-135 spectra, which showed three signals for **1** and two signals for **2** for their pyrrole ring carbon atoms. Furthermore, the FT-IR spectrum of **2** displays the ν(NH) stretching frequency at 3239 cm^{-1} appearing as a strong band, which is absent in the IR spectrum of **1**. These two compounds exhibit different physical properties; compound **1** is highly soluble in common organic solvents such as MeOH, $CHCl_3$, DCM, etc., whereas compound **2** is poorly soluble in these solvents. The pyrrolic N versus α-C regioselectivity could be explained in terms of acidity of the pyrrole-2-carbaldehyde NH group. In the absence of an added acid, the base-catalyzed Mannich reaction mechanism operates [12]. Thus, the piperazine probably abstracts the pyrrolic NH proton and resulting pyrrolidine anion attacks the in situ generated iminium ions present in the mixture to give the N-aminomethylated product. Conversely, in the case of acidic medium, the pyrrolic α-C is active and attacks the iminium ion to give the expected α-C aminomethylated product.

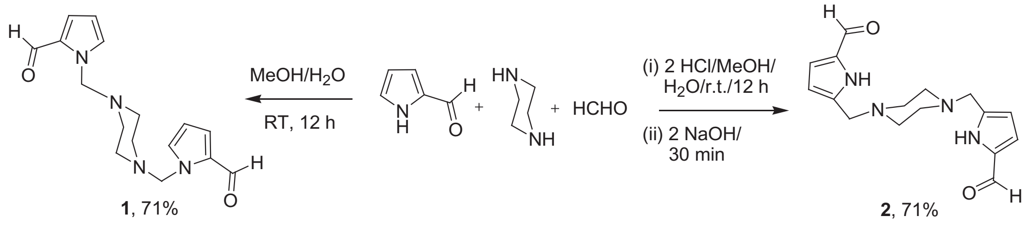
While our attempts to get suitable single crystals of compound **1** have failed, the structure of **2** was confirmed by single crystal X-ray diffraction analysis. The X-ray structure of **2** and the selected bond lengths and angles are given in Fig. 1 and Table 1, respectively. The two pyrrolyl moieties are bound in the equatorial positions of the chair conformation of the piperazine ring. While one of the pyrrolealdehyde moieties with its carbonyl O and the pyrrolic NH groups is oriented in one direction, the same groups in the other side of the molecule are oriented in an opposite direction. This results in four intermolecular hydrogen bonds between these groups for every molecule and formation of the 1D supramolecular chain structure in the crystal lattice (Fig. 1c). This is similar to the hydrogen bonding observed in the structure of *N*,*N*-di(α-formylpyrrolyl-α-methyl)-*N*-methylamine reported by us [13].

2.2. Synthesis and characterization of bis(iminopyrrolyl) ligand

Having synthesized the dialdehyde compounds containing the piperazine ring, we then set the synthesis of their open chain Schiff bases because such bases would provide two sets of donor atoms to a metal atom and give bimetallic complexes. The Schiff base condensation reaction of **2** with two equiv of 2,6-diisopropylaniline in the presence of two equiv of HNO_3 gave the [1+2] condensation product **3** and the partially hydrolyzed [1+1] product **4** in 53% and 20% yields, respectively, after column chromatographic separation (Scheme 2). Conversely, the analogous reaction using **1** resulted in the formation of the monoiminopyrrole compound **5** owing to the hydrolysis of the pyrrolic N–C bond on either side of molecule by nitric acid. While the compound **5** is a known compound [2b], compounds **3** and **4** are new compounds and characterized by spectroscopic methods.

The ^{1}H NMR spectrum of **3** features a sharp singlet at $\delta = 7.85$ ppm for the azomethine protons and at $\delta = 3.65$ ppm for the methylene protons. The pyrrolic NH resonance was not observed owing to an amine-azafulvene tautomeric structure, which forms upon transfer of the pyrrolic NH proton to the basic imine nitrogen atom. Analogous behavior has been reported for the other iminopyrrole molecules reported by us [11]. The FT-IR spectrum shows the ν(CH=N) stretching frequency at 1627 cm^{-1}. In addition, the molecular ion peak [M+H$^+$] at *m*/*z* 619.4512 (calc. mass 619.4488) is observed in the HRMS spectrum. Conversely, the ^{1}H NMR spectrum of **4** features a broad resonance at $\delta = 9.82$ ppm which is assigned to the pyrrolic NH group located adjacent to the aldehyde group, while the other NH resonance does not appear owing to the amine–azafulvene tautomerism. The other resonances and their integrated intensity ratios are in accord with the structure of **4**. Besides, compound **4** shows the molecular ion peak at *m*/*z* 460.3111 (calc. mass 460.3076) corresponding to the mass of its [M+H$^+$] ion in the HRMS spectrum.

The structure of the [1+2] Schiff base **3** was confirmed by the single crystal X-ray diffraction method (Fig. 2). The X-ray structure revealed the typical iminopyrrole form rather than the amine–azafulvene tautomeric structure, as shown by the N1–C13 (1.274 (3) Å) and C13–C14 (1.432(4) Å) distances, corresponding to the double and single bonds, respectively. The molecule possesses two binding cavities for metal atoms. There is no bound water in



Scheme 1. Synthesis of the regioselective dialdehydes **1** and **2** containing the piperazine ring.

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