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The structures of cobalt(II) and copper(II) complexes derived from 6-(4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridine-2-carboxylic acid

Pavel Drabina [a,*], Petr Funk [a], Aleš Růžička [b], Ján Moncol [c], Miloš Sedlák [a]

[a] Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 53210 Pardubice, Czech Republic
[b] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 53210 Pardubice, Czech Republic
[c] Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia

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Dedicated to Professor Josef Panchartek on the occasion of 80th birthday

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A B S T R A C T

6-(4-Isopropyl-1,4-dimethyl-4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridine-2-carboxylic acid (**1**) was used for the preparation of three copper(II) complexes, **5**–**7**, and one cobalt(II) complex, **8**. The structures of these complexes were studied in the solid phase and in solution by means of X-ray diffraction and mass spectrometry. It was found that all the copper(II) complexes exhibit structures in which the copper atom assumes a distorted tetragonal pyramidal configuration. In solution, the neutral complexes **5** and **6** were present as an equilibrium mixture of mononuclear and binuclear forms. In the solid phase, the structures of the complexes differ: complex **5** is monomeric, **6** is polymeric and **7** is a cyclic tetramer. In contrast to that, the cobalt complex **8** was found to be trinuclear, with one cobalt(II) ion being bound covalently with the carboxylic groups of two ligands and assuming an octahedral geometry, while the remaining cobalt atoms are bound coordinatively and their geometries correspond to trigonal bipyramids.

1. Introduction

Transition metal complexes with nitrogen ligands need to be studied in order to explain and understand their physico-chemical properties. At present, the most intensively studied properties of the complexes include, in particular, their catalytic activity in various chemical processes. A significant field in the studies of catalytic properties of coordination compounds containing an optically active compound as the ligand concerns the investigation of their enantio-selectivity [1].

The derivatives of 4,5-dihydro-1*H*-imidazol-5-ones [2], oxazolines [3] and imidazolidin-4-ones [4] studied by us also belong to such chiral nitrogen-containing ligands. For instance, we have dealt with the preparation, structure and catalytic properties of copper(II) complexes of 2-(4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridine [2c] and 2-(pyridin-2-yl)imidazolidin-4-one derivatives [4]. It was found that these complexes are suitable catalysts for the asymmetrical Henry reaction. In spite of the fact that in almost all cases the chemical yields of this catalytic process were excellent, the optical yields were very variable [2c,4]. A significant factor affecting the enantiocatalytic effectiveness of the said complexes is their stability in the given catalytic system and the spatial arrangement of the coordinated species in the ligand field of the metal.

The aim of the work presented here was to modify the earlier described 2-(4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridine ligand, namely the carboxylic acid group at the 6-position of the pyridine cycle (Chart 1). The carboxylic group can form a strongly polarized covalent bond with metal ions, this bond being substantially more stable than a coordination bond. This fact should contribute to a significant increase in the stability of the corresponding metal complexes, which might favourably affect the catalytic properties. These properties of the new compounds will be studied later. The introduction of the carboxylic group transforms the originally *N*,*N*-bidentate ligand into an *O*,*N*,*N*-tridentate ligand, which initiated our more detailed structural investigation of the complexes of this ligand with selected transition metals.

The coordination properties of ligand **1** were studied, particularly with copper(II) salts. In a targeted way, we prepared complexes with copper(II) chloride and bromide, **5** and **6**, respectively; their structures were compared with the recently described copper(II) complexes of 4,5-dihydro-1*H*-imidazol-5-ones. In earlier work [2c] it was found that these complexes can form monomeric and/or dimeric structure(s) depending on the substitution of 4,5-dihydro-1*H*-imidazol-5-ones and the type of halide. Ligand **1** is also structurally very similar to substituted 6-(1,3-oxazolin-2-yl)pyridine-2-carboxylates, and in this case it was found [3] that their complexes with

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* Corresponding author. Tel.: +420 466 037 010; fax: +420 466 037 068.
E-mail address: pavel.drabina@upce.cz (P. Drabina).

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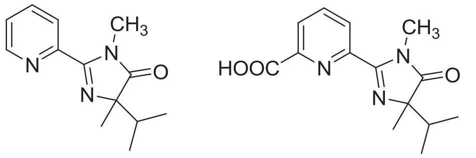


(±)-**1**
(*R*)-(+)-**1**
(*S*)-(−)-**1**

Chart 1. 2-(4,5-Dihydro-1*H*-imidazol-5-on-2-yl)pyridine ligands.

copper(II) chloride and bromide form polymeric super-molecular arrangements in the solid phase. Moreover, the cobalt(II) complex **8** was also prepared for comparison: its structure was expected to differ from that of the copper(II) complexes **5** and **6**.

2. Experimental

2.1. General procedure

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500.13 (^{1}H) and 125.76 MHz (^{13}C) in d_6-DMSO. The ^{1}H and ^{13}C chemical shifts were referenced to the central peaks of the solvent ($\delta = 2.50$ and 39.51, respectively). The mass spectra were recorded on an instrument set from Agilent Technologies (gas chromatograph 6890N with mass detector 5973 Network) and mass spectra of complexes were measured on a VG Platform II mass spectrometer (Micromass, Manchester, UK) with chemical ionization at atmospheric pressure (APCI) and a quadrupole analyzer (0–3000 Da). For the mobile phase acetonitrile was used. The elemental analyses were performed on a FISONS Instruments EA 1108 CHN. The optical rotation was measured on a Perkin-Elmer 341 instrument, values are given in 10^{-1} deg cm^{2} g^{-1}. FT-IR spectra were recorded on a Perkin-Elmer Spectrum BX.

2.2. Synthesis of the ligand

Racemic and optically pure 2-amino-2,3-dimethylbutanamides were prepared according to the method reported by Wepplo [5]. 6-Methoxycarbonylpyridine-2-carboxylic acid was prepared according to the previously described procedure [6]. The other reagents and solvents were purchased from commercial sources and were used without further purification. The compounds **2**–**4** were synthesized according to our previously reported procedures (Scheme 1) [2].

2.2.1. (±)-N-[2-Carbamoyl-3-methyl)butyl]-6-methoxycarbonylpyridine-2-carboxamide [(±)-**2**]

Yield: 84%; mp 193–196 °C (THF); ^{1}H NMR (DMSO) δ: 8.88 (1 H, brs, NH), 8.26 (3H, m, Py), 7.41 (1H, brs, NH$_2$), 7.23 (1H, brs, NH$_2$), 3.98 (3H, s, OCH$_3$), 2.35 (1H, sp, $J = 6.9$ Hz, *i*PrCH), 1.63 (3H, s, CH$_3$), 1.02 (3H, d, $J = 6.9$ Hz, *i*PrCH$_3$), 0.96 (3H, d, $J = 6.9$ Hz, *i*PrCH$_3$); ^{13}C NMR (DMSO) δ: 174.4, 164.5, 161.8, 150.5, 146.2, 139.7, 127.3, 124.8, 62.5, 52.9, 34.6, 18.0, 17.5, 17.4. *Anal.* Calc. for $C_{14}H_{19}N_3O_4$: C, 57.32; H, 6.54; N, 14.33. Found: C, 57.24; H, 6.78; N, 14.34%.

2.2.2. (R)-N-[2-Carbamoyl-3-methyl)butyl]-6-methoxycarbonylpyridine-2-carboxamide [(R)-(−)-**2**]

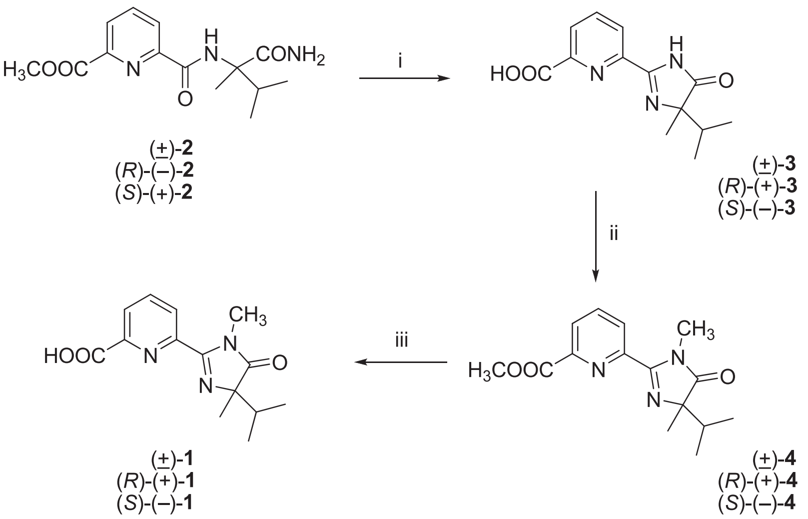
Yield: 81%; mp 211–213 °C (THF); $[\alpha]_{\mathrm{D}}^{20}$ −9.1 (*c* 0.32 in CH$_3$OH); ^{1}H NMR (DMSO) δ: 8.88 (1H, brs, NH), 8.28 (3H, m, Py), 7.41 (1H, brs, NH$_2$), 7.23 (1H, brs, NH$_2$), 3.98 (3H, s, OCH$_3$), 2.35 (1H, sp, $J = 6.5$, *i*PrCH), 1.62 (3H, s, CH$_3$), 1.02 (3H, d, $J = 6.5$, *i*PrCH$_3$), 0.95 (3H, d, $J = 6.9$, *i*PrCH$_3$); ^{13}C NMR (DMSO) δ: 174.4, 164.5, 161.8, 150.5, 146.2, 139.7, 127.3, 124.8, 62.5, 52.9, 34.6, 18.0, 17.5, 17.4. *Anal.* Calc. for $C_{14}H_{19}N_3O_4$: C, 57.32; H, 6.54; N, 14.33. Found: C, 57.35; H, 6.61; N, 14.38%.

2.2.3. (S)-N-[2-Carbamoyl-3-methyl)butyl]-6-methoxycarbonylpyridine-2-carboxamide [(S)-(+)-**2**]

Yield: 82%; mp 205–207 °C (THF); $[\alpha]_{\mathrm{D}}^{20}$ +9.4 (*c* 0.36 in CH$_3$OH); ^{1}H NMR (DMSO) δ: 8.87 (1H, brs, NH), 8.26 (3H, m, Py), 7.40 (1H, brs, NH$_2$), 7.22 (1H, brs, NH$_2$), 3.98 (3H, s, OCH$_3$), 2.35 (1H, sp, $J = 6.5$, *i*PrCH), 1.63 (3H, s, CH$_3$), 1.02 (3H, d, $J = 6.5$, *i*PrCH$_3$), 0.95 (3H, d, $J = 6.9$, *i*PrCH$_3$); ^{13}C NMR (DMSO) δ: 174.4, 164.5, 161.8, 150.5, 146.2, 139.7, 127.3, 124.8, 62.5, 52.9, 34.6, 18.0, 17.5, 17.4. *Anal.* Calc. for $C_{14}H_{19}N_3O_4$: C, 57.32; H, 6.54; N, 14.33. Found: C, 57.37; H, 6.58; N, 14.13%.

2.2.4. (±)-6-(4-Isopropyl-4-methyl-1H-imidazol-5-on-2-yl)pyridine-2-carboxylic acid [(±)-**3**]

Yield: 83%; mp 199–202 °C (CH$_2$Cl$_2$); ^{1}H NMR (DMSO) δ: 12.83 (1 H, brs, COOH), 11.73 (1H, brs, NH), 8.47 (1H, dd, $J = 7.4$, $J = 1.1$, Py(3)H), 8.28 (2H, m, Py(4,5)H), 2.02 (1H, sp, $J = 6.6$, *i*PrCH), 1.34 (3H, s, CH$_3$), 1.04 (3H, d, $J = 6.6$, *i*PrCH$_3$), 0.84 (3H, d, $J = 6.6$, *i*PrCH$_3$); ^{13}C NMR (DMSO) δ: 181.3, 164.3, 163.4, 147.4, 141.7, 140.3, 128.7,



(±)-**2**
(*R*)-(−)-**2**
(*S*)-(+)-**2**

(±)-**3**
(*R*)-(+)-**3**
(*S*)-(−)-**3**

(±)-**1**
(*R*)-(+)-**1**
(*S*)-(−)-**1**

(±)-**4**
(*R*)-(+)-**4**
(*S*)-(−)-**4**

Scheme 1. *Reagents and conditions:* (i) 1. NaOH/H$_2$O, rt, 48 h; 2. HCl; (ii) CH$_3$I/*t*-BuOK, DMF, rt, overnight; (iii) 1. NaOH/H$_2$O, rt, 3 h; 2. HCl.