



# Preparation, structures and antimicrobial activity of four different type metal complexes on the base of diethanolamine and *o*-nitrobenzoic acid



A.B. Ibragimov <sup>a,\*</sup>, J.M. Ashurov <sup>b</sup>, B.T. Ibragimov <sup>b</sup>, B.S. Zakirov <sup>a</sup>

<sup>a</sup> Institute of General and Inorganic Chemistry of AS, M. Ulugbek Str., 77a, Tashkent, 100125, Uzbekistan

<sup>b</sup> Institute of Bioorganic Chemistry of AS, M. Ulugbek Str., 83, Tashkent, 100125, Uzbekistan

## ARTICLE INFO

### Article history:

Received 21 April 2016

Received in revised form

29 August 2016

Accepted 29 August 2016

Available online 31 August 2016

### Keywords:

Diethanolamine

*o*-Nitrobenzoic acid

Metal complex

Organic salt

X-ray crystallography

Antimicrobial activity

## ABSTRACT

Crystallization under identical conditions from aqueous ethanol solutions of diethanolamine (DEA), *o*-nitrobenzoic acid (ONBA) and definite metal salt yields 4 different type metal complexes and one organic salt – the monoligand complex of Zn(II) with DEA (**1**), monoligand complex of Cu(II) with ONBA (**2**), mixed-ligand complex of Ni(II) with DEA and ONBA (**3**), supramolecular complex between monoligand complex molecule of Zn(II) with DEA and ONBA (**4**) and DEA<sup>+</sup>·ONBA<sup>-</sup> salt (**5**). In **1** two meridionally distributed DEA molecules are coordinated by a tridentate mode, **2** is a binuclear copper complex with 4 ONBA molecules which are bidentately coordinated through carboxylate groups. In **3** two DEA and two ONBA molecules are coordinated by bidentate and monodentate fashions, respectively. The compound **4** consists of a complex molecule with two facial distributed tridentate DEA molecules and ONBA ones in an outer sphere. Hence, in coordination compounds **1** and **4** Zn-complex ions with two tridentately coordinated DEA molecules are found in different isomeric forms of which a *mer*-distribution is recorded for the first time. The maximal enhancement of the ligands antimicrobial activity is observed for the mixed-ligand metal complex. The Zn-complex with *mer*-distributed ligand molecules demonstrated more antimicrobial activity in contrast to *fac*-isomer.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Reaction media containing dissolved metal (M) salt and two ligands L1 and L2 may yield different types of metal complexes featuring with different composition and coordination structure, such as M(L1), M(L2), M(L1 + L2), M(L1)·L2, M(L2)·L1 and *etc.* The type of the produced complexes is dictated by reaction conditions including a ratio of reagents, concentration, pH, temperature, kinetics of the process and type of metal salt. It is of a great fundamental interest to establish how many types of coordination complexes may be obtained on the base of the definite pair of ligands if preparation conditions will be kept identical for different metal salts. Moreover, such research is also of a practical interest owing to possibility to enhance some properties of the starting substances in the obtained compounds, *e.g.* biological activity of the ligands by a preparation of the definite type metal complexes [3],

mostly mixed-ligand coordination complexes [4,5]. Of course, for this purpose both of ligands should demonstrate the same bioactivity.

Therefore we are carrying out a systematic research using as ligands ethanolamines [1] and mono-substituted benzoic acids such as amino-, hydroxy- and nitrobenzoic acids [10] which are well-known, easily available, not expensive substances and characterized by moderate biological activity as antimicrobial compounds [2,9]. Ethanolamines easily form chelated metal complexes and may inhibit an involvement of the not chelating benzoic acids to coordination sphere [6–8].

Indeed, our researches showed that, for example, triethanolamine (L1) shared sites of the coordination sphere of Cu(II), Zn(II) and Cd(II) with *p*-nitrobenzoic acid (L2) giving rise to the totally different mixed-ligand complexes of M(L1 + L2) type [11] but *m*-hydroxybenzoic acid was retained in an outer sphere of the Ni(II)-ion yielding M(L1)·L2 type complex [12]. The same type complex M(L1)·L2 of Mn(II) is obtained in case of the diethanolamine (DEA) and *m*-aminobenzoic acid ligand pair [13].

On example of the DEA and *o*-nitrobenzoic acid (ONBA) ligand

\* Corresponding author.

E-mail address: [aziz\\_ibragimov@mail.ru](mailto:aziz_ibragimov@mail.ru) (A.B. Ibragimov).

pair, however, we could prepare under the same conditions four different type complexes and one organic salt between ligands. We are reporting here a preparation, molecular and crystal structures and antimicrobial activity of these compounds -  $[\text{Zn}(\text{DEA})_2] \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$  (**1**),  $[\text{Cu}_2(\text{ONBA})_4 \cdot (\text{H}_2\text{O})_2] \cdot 2(\text{EtOH})$  (**2**),  $\text{Ni}[(\text{DEA})_2 + (\text{ONBA})_2] \cdot \text{H}_2\text{O}$  (**3**),  $[\text{Zn}(\text{DEA})_2] \cdot 2(\text{ONBA})$  (**4**) and  $\text{DEA} \cdot \text{ONBA}$  (**5**).

## 2. Experimental

### 2.1. General methods and materials

All reagents were readily available from commercial sources and were used as received without further purification. Analyses of C, H and N were performed on a German Elementar Vario EL instrument. Data for the crystal structure determinations were collected at 293 K on an "Oxford Diffraction Xcalibur-R CCD diffractometer" ( $\text{CuK}\alpha$ -radiation,  $\lambda = 1.54184 \text{ \AA}$ ,  $\omega$ -scan mode, graphite monochromator). IR-spectra were registered in the 4000–400  $\text{cm}^{-1}$  range on FTIR Nicolet iS50 (Thermo Scientific, USA) equipment. For registration of mass spectra the QQQ<sup>®</sup> 6420 LC/MS/MS triple quad mass spectrometer (Agilent Technologies, USA) was used.

### 2.2. Preparation of the complexes

#### 2.2.1. The synthesis of $[\text{Zn}(\text{DEA})_2] \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$ (**1**)

To an aqueous solution (3 ml) of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (0.143 g, 0.5 mmol) was slowly added an ethanol solution (5 ml) containing DEA (96  $\mu\text{L}$ ) and ONBA (0.167 g, 1 mmol) with constant stirring. After 17 days a crystalline product was obtained at room temperature by solvent evaporation. Yield: 60%. Elemental analysis: Calc. for  $\text{C}_8\text{H}_{24}\text{N}_2\text{O}_9\text{SZn}$  (389.72) – C, 24.65; H, 6.21; N, 7.18. Found – C, 24.58; H, 6.31; N, 7.22%. FTIR ( $\text{cm}^{-1}$ ): 3204m ( $\nu$ -OH), 2929 w ( $\nu^{\text{as}}$ -CH<sub>2</sub>), 2644 br, 1560 m ( $\delta$ -NH), 1534 s, 1521 s, 1480 s ( $\delta$ -CH<sub>2</sub>), 1459 m, 1443 m, 1389 s, 1371 s, 1345 vs, 1297 m, 1260 w, 1250 w, 1223 w, 1137 w, 1108m, 1075 w, 1018 vs ( $\text{SO}_4$ ), 963 w, 869 m, 858 s, 813 m, 794 s, 781 m, 744s, 692 s, 647 s ( $\text{SO}_4^{2-}$ ), 545 w, 522 w, 468 w, 436 s (Zn–N).

#### 2.2.2. The synthesis of $[\text{Cu}_2(\text{ONBA})_4 \cdot (\text{H}_2\text{O})_2] \cdot 2(\text{EtOH})$ (**2**)

An ethanol solution (5 ml) containing DEA (96  $\mu\text{L}$ ) and ONBA (0.167 g, 1 mmol) was slowly added with constant stirring to an aqueous solution (3 ml) of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.124 g, 0.5 mmol). The crystalline product was obtained by solvent evaporation after 16 days (room temperature). Yield: 55%. Elemental analysis: Calc. for  $\text{C}_{32}\text{H}_{32}\text{N}_4\text{O}_{20}\text{Cu}_2$  (919.69) – C, 41.78; H, 3.51; N, 6.09. Found – C, 41.54; H, 3.42; N, 6.15%. FTIR ( $\text{cm}^{-1}$ ): 3074 br, 1648 w, 1606 m, 1522 vs ( $\nu^{\text{as}}$ -NO<sub>2</sub>), 1484 m, 1443 w, 1406 s ( $\nu^{\text{s}}$ -COO<sup>-</sup>), 1350 s ( $\nu^{\text{s}}$ -NO<sub>2</sub>), 1308 w, 1076 s, 1058 s, 1035 s, 863 w, 838 w, 781 s, 738 s, 700 s, 650 s, 608 w, 553 w, 480 s (Cu–O), 429 w.

#### 2.2.3. The synthesis of $\text{Ni}[(\text{DEA})_2 + (\text{ONBA})_2] \cdot \text{H}_2\text{O}$ (**3**)

To an aqueous solution (3 ml) of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.145 g, 0.5 mmol) was slowly added an ethanol solution (5 ml) containing DEA (96  $\mu\text{L}$ ) and ONBA (0.167 g, 1 mmol) with constant stirring. The crystalline product was obtained at room temperature by solvent evaporation after 18 days. Yield: 52%. Elemental analysis: Calc. for  $\text{C}_{44}\text{H}_{62}\text{N}_8\text{O}_{25}\text{Ni}_2$  (1220.43) – C, 43.31; H, 5.12; N, 9.18. Found – C, 43.25; H, 5.19; N, 9.22%. FTIR ( $\text{cm}^{-1}$ ): 3324 m ( $\text{H}_2\text{O}$ ), 3276 m (OH), 2938 w (CH<sub>2</sub>), 2895 w, 1584 w ( $\nu^{\text{as}}$ -COO<sup>-</sup>), 1527 w ( $\nu^{\text{as}}$ -NO<sub>2</sub>), 1472 w, 1402 m ( $\nu^{\text{s}}$ -COO<sup>-</sup>), 1352 vs ( $\nu^{\text{s}}$ -NO<sub>2</sub>), 1327 s (C–OH), 1281 m, 1118 m, 1030 s, 863 w, 825 m, 810 w, 786 w, 774 w, 728 w, 708 w, 696 w, 647 m, 590 w, 556 w, 516 w, 487 w (Ni–N), 406 w.

#### 2.2.4. The synthesis of $[\text{Zn}(\text{DEA})_2] \cdot 2(\text{ONBA})$ (**4**)

An ethanol solution (5 ml) containing DEA (96  $\mu\text{L}$ ) and ONBA (0.137 g, 1 mmol) was slowly added to an aqueous solution (3 ml) of  $\text{Zn}(\text{CH}_3\text{OO})_2 \cdot 2\text{H}_2\text{O}$  (0.097 g, 0.5 mmol) with constant stirring. After filtration, the solution was left to stand at room temperature. Crystals of the complexes were obtained by solvent evaporation after 20 days. Yield: 55%. Elemental analysis: Calc. for  $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_6\text{Zn}_{0.5}$  (302.70) – C, 43.43; H, 4.93; N, 9.21. Found – C, 43.53; H, 4.85; N, 9.30%. FTIR ( $\text{cm}^{-1}$ ): 3245 m ( $\nu$ -OH), 2936 br (CH<sub>2</sub>), 2645 br, 1586 m ( $\delta$ -NH), 1561 s ( $\nu^{\text{as}}$ -COO<sup>-</sup>), 1529 s ( $\nu^{\text{as}}$ -NO<sub>2</sub>), 1479 w ( $\delta$ -CH<sub>2</sub>), 1438 m, 1379 s, 1359 vs ( $\nu^{\text{s}}$ -NO<sub>2</sub>), 1294 m, 1247 m, 1219 w, 1136 w, 1109 m, 1077 w, 1019 s, 1007 m, 965 w, 898 w, 871 m, 807 m, 779 m, 732 s, 693 s, 641 m, 584 w, 555 w, 527 w, 469 m (Zn–N), 436 m.

#### 2.2.5. The synthesis of $\text{DEA} \cdot \text{ONBA}$ (**5**)

To an aqueous solution (3 ml) of  $\text{Cd}(\text{CH}_3\text{OO})_2$  (0.103 g, 0.5 mmol) was slowly added an ethanol solution (5 ml) containing DEA (96  $\mu\text{L}$ ) and ONBA (0.167 g, 1 mmol) with constant stirring. The crystalline product was obtained at room temperature by evaporation of solvent after 18 days. Yield: 53%. Elemental analysis: Calc. for  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_6$  (272.26) – C, 48.53; H, 5.92; N, 10.28. Found – C, 48.44; H, 5.88; N, 10.34%. FTIR ( $\text{cm}^{-1}$ ): 3426 m (OH), 3087 m, 2953 s, 2925 vs ( $\nu^{\text{as}}$ -CH<sub>2</sub>), 2868 s ( $\nu^{\text{s}}$ -CH<sub>2</sub>), 2671 m ( $\text{NH}^+$ ), 2549 m, 1681 vs, 1606 s, 1535 vs ( $\nu^{\text{as}}$ -NO<sub>2</sub>), 1489 s ( $\delta$ -CH<sub>2</sub>), 1449 m, 1417 m ( $\nu^{\text{s}}$ -COO<sup>-</sup>), 1366 s ( $\nu^{\text{s}}$ -NO<sub>2</sub>), 1292 s, 1141 m, 1073 m, 1007 w, 975 w, 915 m, 861 m, 796 s, 781 s, 731 s, 688 s, 643 w, 583 w, 553 m.

### 2.3. X-ray structure analysis

Experimental data were collected using the CrysAlisPro program [14]. An absorption correction was applied by the multi-scan method using the same program. The structures were solved by a direct method of the SHELXS-97 program package [15] and refined by full-matrix least squares using the SHELXL-97 program [16]. All none hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters, except for the hydrogen atoms of some hydroxyl groups, which were located in a Fourier-difference map and refined isotropically. The molecular drawings were plotted by MERCURY program package [17]. The crystallographic data and details of structure refinement of compounds (except **3**) are given in Table 1.

The determination of the crystal structure of compound **3** was associated with a great problem. The unit cell of the monoclinic crystal with space group  $\text{P}2_1/\text{c}$  contains two Ni(II) mixed-ligand complex ions and one water molecule. The structure refinement is not progressed below  $R = 24.90\%$  even for different data collections from three single crystals. Efforts for refinement using TwinRotMat program of a multipurpose crystallographic tool PLATON also failed. Therefore, in order to be confident on these results we have involved the LC ESI-MS analyses.

### 2.4. Mass-spectrometry

For a registration of the spectra by ESI-MS/MS analysis the small mono-crystal has been dissolved in 100% HPLC grade MeOH solvent. Source parameters (e.g., temperatures, gas flows, etc.) were optimized. Mass spectra were registered in positive and negative modes over the range of  $m/z$  40–650; the flow rate of the nitrogen gas was 10 ml/min at a temperature of 300 °C, the gas pressure on the needle nebulizer – 20 psi, fragmentor voltage – 30 V and capillary one – 3500 V.

Download English Version:

<https://daneshyari.com/en/article/7809179>

Download Persian Version:

<https://daneshyari.com/article/7809179>

[Daneshyari.com](https://daneshyari.com)