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THE STRUCTURE AND SPECTROSCOPIC CHARACTERIZATION OF COORDINATION COMPOUNDS WITH α -PHENYL-N-METHYLNITRONE IN SOLUTION AND IN SOLID STATE

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New coordination compounds of α -phenyl-N-methylnitrone with Cu^{2+} , Mn^{2+} , Ni^{2+} , and UO_2^{2+} were synthesized. Complexes were studied by means of IR, NMR and UV-Vis spectroscopies. The crystal and molecular structure of uranyl complex with α -phenyl-N-methylnitrone was determined by X-ray diffraction study. The monodentate nitrone ligands are coordinated to the metal ion via oxygen atom. The coordination polyhedron of uranium is a distorted hexagonal bipyramide. It was shown that there is dynamic process in the acetone solution in the temperature range of 203–297 K. The ligand exists as a trans-isomer for both present forms of organic ligand by the NOE difference. Dimeric copper(II) benzoate was obtained via recrystallization of the copper complex with α -phenyl-N-methylnitrone from methanol solution. According to X-ray diffraction analysis, the environment of each of the copper atoms is octahedral. The coordination sphere is formed by six oxygen atoms. Three anions of benzoic acid are coordinated bidentate-bridged through oxygen atoms of the carboxyl group, while one molecule of benzoic acid is coordinated monodentatically through the carboxyl oxygen atom.

Keywords: nitrone, complex, uranyl, crystal structure, NMR spectroscopy.**DOI:** 10.32434/0321-4095-2022-140-1-88-94

Introduction

The considerable interest of researchers in the organic chemistry of nitrones is caused by a diversity of their chemical properties and synthetic utility [1–4]. These compounds can react with both nucleophiles and electrophiles in addition and substitution reactions due to their electronic structure [3–5]. They find application as spin traps for the study of various processes in biological systems [6]. High electron density on the oxygen atom of the nitrone group facilitates the complex formation, but the coordination chemistry of this class of compounds is largely unexplored. There are a number of papers devoted to the study of complexation both transition metals [7,8] and non-transition metals [9]. Usually, these are multi-ligand complexes where the derivatives of acetylacetonates, porphyrin, and others serve as additional ligands.

Earlier we studied the coordination properties of five-membered heterylnitrones, namely C-2-thiophene-N-methylnitrone, C-2-furan-N-methylnitrone and C-2-pyrrole-N-methylnitrone

[10,11]. Herein, we describe the synthesis and characterization of coordination compounds with α -phenyl-N-methylnitrone, as a simplest representative of aromatic nitrones.

Experimental

Solvents were used as supplied or were distilled using standard methods. Reagents were purchased from Aldrich or Fluka. The IR spectra (KBr, pellet) were recorded with Spectrum BX Perkin Elmer spectrometer. Absorption spectra were measured using a UV-2800 spectrophotometer (Unico, USA). ^1H NMR spectra were recorded on Bruker Avance DPX300 spectrometer. Electroconductivity measurements for uranyl complex were made at room temperature in acetone solutions in the concentration range of 0.02 to 0.002 mol l^{-1} . Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Analyzer.

X-ray diffraction data for compound 4 (see below) were collected with an Enraf-Nonius CAD4 diffractometer. An empirical absorption correction based on azimuthal scan data was applied. The

structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation using the CRYSTALS program package [12]. All hydrogen atoms were located in the different Fourier maps and refined isotropically.

Crystal data for the $\text{Cu}(\text{Benzoat})_4(\text{Hbenzoat})_2$ (5) were collected using a KM4CCD area detector diffractometer. The structure was solved by direct methods and refined by the least-square method using the programs SHELXS and SHELXL-93 [13]. All the non-hydrogen atoms were refined anisotropically.

The crystallographic parameters and summary of data collection for compounds 4 and 5 are listed in Table 1. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center and are available on request quoting the depository numbers CCDC- 204911 and CCDC-204910 for 4 and 5, respectively.

Synthesis of ligand and metal complexes (1)–(4)

The starting materials for the synthesis of α -phenyl-N-methylnitron (L) were commercially available benzaldehyde and N-methylhydroxylamine hydrochloride. The ligand L was prepared according to the standard procedure [1] (m.p. 82–84°C).

Complex compounds were synthesized through the following reaction:

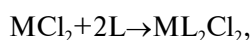
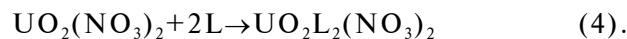


Table 1
Selected crystal data and structure refinement parameters of 4 and 5

Parameter	Value or characteristic	
Empirical formula	$\text{C}_{16}\text{H}_{18}\text{UO}_{10}\text{N}_4$	$\text{C}_{42}\text{H}_{32}\text{Cu}_2\text{O}_{12}$
Molecular weight	332.18	855.8
Crystal system	monoclinic	monoclinic
Space group	$\text{P}2_1/\text{n}$	$\text{P}2_1/\text{n}$
a, Å	7.765(3)	10.795(2)
b, Å	13.325(3)	11.536(2)
c, Å	10.392(2)	15.096(3)
β , °	100.41(2)	90.87(3)
V , Å ³	1057.5	1879.7(6)
Z	1	2
D_{calc} , mg mm ⁻³	2.09	1.229
μ , mm ⁻¹	7.33	1.179
Crystal size, mm ³	0.26×0.34×0.4	0.22×0.3×0.4
θ_{min} , θ_{max} , °	0 to 30	3.53 to 28.39
Reflections collected	3082	4351
Independent reflections	1352	3693
GOF	1.044	1.131
R_1 ($I > 2\sigma(I)$)	0.0525	0.0448
wR_2 (all data)	0.0560	0.0883

where M= Cu^{2+} (1), Mn^{2+} (2), and Ni^{2+} (3);



ML_2Cl_2

All compounds of 3d-metals were prepared by the same procedure. For example, in a typical synthesis, a solution of copper chloride $\text{CuCl}_2 \cdot 2.06\text{H}_2\text{O}$ (0.04 g, 0.23 mmol) in mixture of acetonitrile:methanole (10:1) (~5 ml) was added to a hot solution of the ligand (0.06 g, 0.46 mmol) in acetonitrile (~3 ml) at stirring. After cooling, brown microcrystals of CuL_2Cl_2 (1) were collected and washed with acetonitrile. Yield 0.057 g (60.8%). IR UV/vis (CH_3CN): λ_{max} (ϵ_{max})=460 nm (660). IR (KBr): $\nu=1640$ (C=N), 1145 (N–O). $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{CuN}_2\text{O}_2$ (404.77): calcd. C 47.47, H 4.48, N 6.92, Cu 15.70; found: C 47.81, H 4.32, N 6.84, Cu 15.62.

MnL_2Cl_2 (2)

Orange microcrystalline powder. UV/vis (CH_3CN): λ_{max} (ϵ_{max})=440 nm (40). IR (KBr): $\nu=1620$ (C=N), 1160 (N–O). Yield 70.2%. $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{MnN}_2\text{O}_2$ (396.16): calcd. C 48.51, H 4.58, N 7.07; found: C 48.59, H 4.75, N 7.43.

NiL_2Cl_2 (3)

Red microcrystalline powder. UV/vis (CH_3CN): λ_{max} (ϵ_{max})=570 nm (31), 620 nm (47), 670 nm (29). IR (KBr): $\nu=1625$ (C=N), 1160 (N–O). Yield 42.4%. $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{NiN}_2\text{O}_2$ (399.91): calcd. C 48.05, H 4.54, N 7.01; found: C 47.92, H 4.48, N 7.21.

$\text{UO}_2\text{L}_2(\text{NO}_3)_2$ (4)

A solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.251 g, 0.5 mmol) in acetonitrile (4 ml) was added to a solution of L (0.135 g, 1 mmol) in acetonitrile (6 ml). The mixture was allowed standing at room temperature in a vacuum desiccator over CaCl_2 for ~40 h. The resulting yellow crystalline precipitate was filtered off, washed with cold acetonitrile, and dried over CaCl_2 . Yield: 0.282 g (85%). IR (KBr): $\nu=1630$ (C=N), 1160 (N–O). $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_{10}\text{U}$ (664.34): calcd. C 28.92, H 2.73, N 8.44; found: C 28.33, H 2.53, N 8.67.

Results and discussion

Infrared spectra

The IR spectra of the coordination compounds are very similar. Infrared spectra of the complexes show a single strong absorption in the 1145–1170 cm^{-1} region which has been assigned to N–O stretching frequency [8]. The $\nu(\text{C}=\text{N})$ vibration is seen at 1620–1640 cm^{-1} . The $\nu(\text{C}=\text{N})$ frequency is increased by 35–50 cm^{-1} and $\nu(\text{N}=\text{O})$ frequency is lowered by 10–35 cm^{-1} with respect to the α -phenyl-

N-methylnitron. The observed shifts are in agreement with the coordination of the nitron to the metal atoms through the oxygen atom [8].

Electronic spectra

Electronic spectra of 1–3 were studied in acetonitrile at ambient temperature. Thus, the spectra of 1 show a band maximum at 460 nm ($\epsilon=660$) and the spectra of 2 show a band maximum at 440 nm ($\epsilon=40$). This spectral feature is characteristic of four-coordinate complexes. Complex 3 exhibits a visible bands at 570 nm ($\epsilon=31$), 620 nm ($\epsilon=47$) and 670 nm ($\epsilon=29$). The spectral features are testified to the presence of different coordination parts in a solution. At the same time, the diffuse reflectance spectrum of the complex 3 exhibited an absorption in the visible region at ~ 500 nm, which corresponds to a d–d transition in a square planar environment around nickel(II). The band at ~ 360 nm is a charge transfer band that observable in the diffuse reflectance spectrum of the low-spin complex of nickel(II).

The green single crystals of compound $\text{Cu}_2(\text{Benzoat})_4(\text{HBenzoat})_2$ (5) (Hbenzoat – benzoic acid) were obtained at recrystallization of complex 1 from methanol. The IR spectrum of 5 shows carboxylate bands at 1610 cm^{-1} for $\nu_{\text{asym}}(\text{OCO})$ and 1400 cm^{-1} for $\nu_{\text{sym}}(\text{OCO})$. The complex $\text{Cu}_2(\text{Benzoat})_4(\text{HBenzoat})_2$ has a dimeric molecular array (Fig. 1). The copper atom has a significantly distorted octahedral environment. Four anions of the benzoic acid are coordinated in a bidentate-bridging fashion. Two molecules of the benzoic acid are coordinated monodentatically. This compound is isostructural with respect to compounds obtained directly from copper carbonate and benzoic acid [14] as well as copper nitrate and benzoic acid [15].

It is well known that nitrones are able to

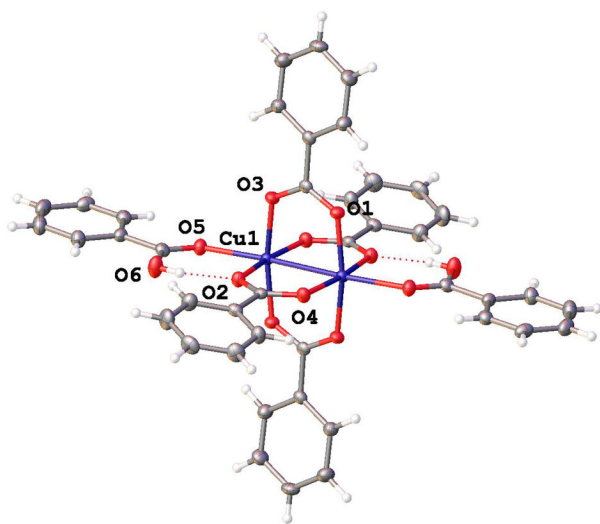
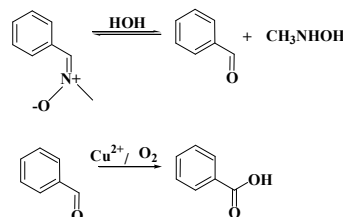


Fig. 1. Molecular structure of 5

decompose under certain condition (pH, hv) yielding starting components: aldehyde and corresponding N-hydroxylamine derivative. In our case, benzaldehyde is oxidized to benzoic acid under the influence of air oxygen and moisture. In one's turn, the ions of metals can provide catalytic activity in oxidation reaction. The reactions may occur in the solution according to Scheme 1.



Scheme 1. Decomposition of the α -phenyl-N-methylnitron to benzoic acid

NMR spectroscopy

The ^1H NMR spectra of complex 4 show a low-field shift of $\text{CH}=\text{N}$ and N-methyl group for 0.7 ppm and 0.3 ppm, respectively. The broadening of signals from $\text{CH}=\text{N}$ and CH_3 can be explained by the presence of some exchange interaction in acetone solution. This dynamic process can be concerned both with ligand isomerism and with rearrangement in the coordination sphere. This question has been further examined by NMR experiment at low temperature (Fig. 2). Thus, a very broad signal appeared for all protons at 253 K and it became sharper at 203 K. Double set of signals for the protons of the ligand can be seen at this temperature. Is this related to the presence of cis-, trans- isomers of the ligand? This question has been further examined by the NOE difference (Fig. 3). We can conclude that L behaves as trans-isomer and NOEs are observed for the azomethyne and methyl protons for both present forms of organic ligand. Thus, observed dynamic process does not relate to isomerism of the ligand, but apparently induced the rearrangement in the coordination sphere, for example, a dissociation process. Let us concentrate on this in more detail. Dissociative process can be concerned with dissociation complex removal organic part (1) as well as nitrate groups (2) (Scheme 2). In case of (1), we observed in NMR spectrum signals from protons of free ligand, but this did not occur. Electroconductivity measurements for 4 were made at room temperature in acetone solution in the concentration range $0.02\text{--}0.002\text{ mol l}^{-1}$ for elucidation of dissociation of the nitrate groups (2). It was shown that the acetone solutions of $\text{UO}_2\text{L}_2(\text{NO}_3)_2$ are weak electrolytes ($C=2.0\cdot 10^{-2}\text{--}$

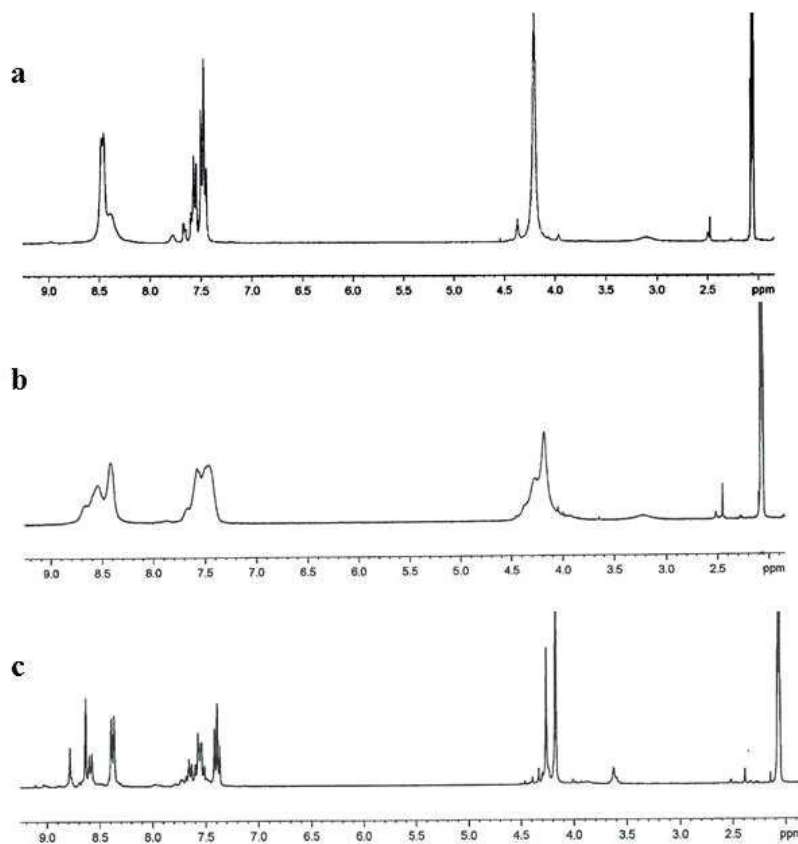


Fig. 2. ^1H NMR spectra of 4 obtained at 297 K (a), 253 K (b) and 203 K (c) in acetone- d_6

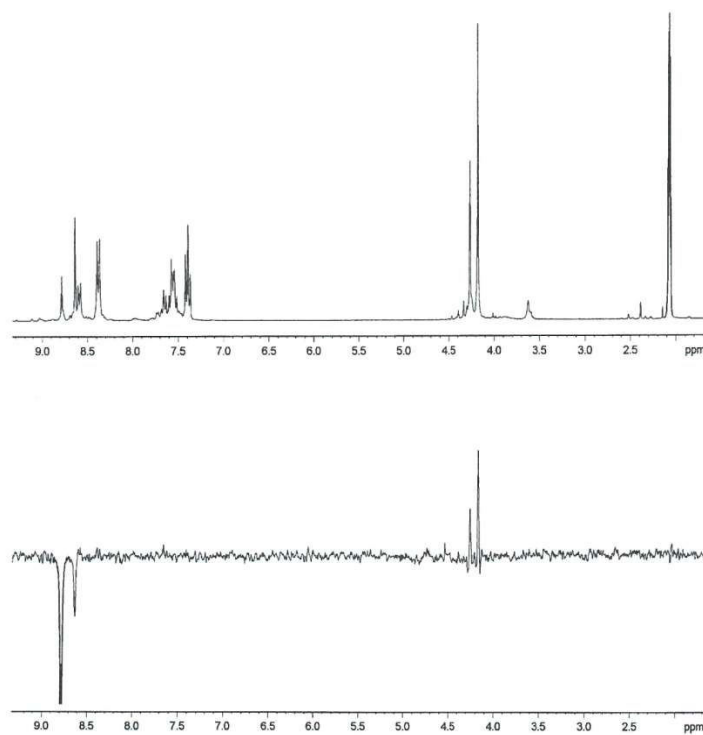
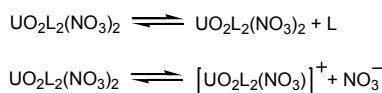


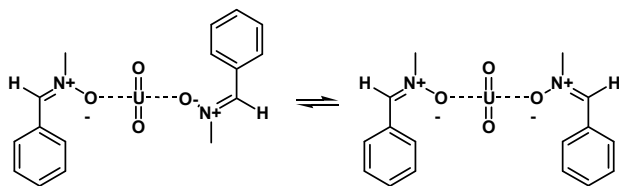
Fig. 3. 1D NOESY experiment with selective excitation azomethine proton (bottom) and ^1H NMR spectra (top) of 4 obtained at -70°C

$0.2 \cdot 10^{-2} \text{ mol l}^{-1}$, $\lambda = 15\text{--}19 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$), therefore very probably the structure of the coordination unit is preserved in acetone and the observed dynamic process do not induce the dissociative process.



Scheme 2. Claimed dissociative processes of 4

The dynamic process that we observe in our system is caused by a very rapid change in the position of the phenyl rings relative to the equatorial plane of uranium at ambient temperature (Scheme 3). It is expected that the rotational speed of the phenyl groups decreases with decreasing temperature. At 253 K, all signals are significantly widened. As the temperature decreases further, the signals begin to coalesce. As mentioned above, a double set of signals is observed in the spectrum at 203 K, which corresponds to the two «extreme» positions of the phenyl ring.



Scheme 3. Rotation of phenyl rings in the complex 4 (nitrate groups are not shown for clarity)

Description of the structure 4

The coordination sphere of U in $\text{UO}_2\text{L}_2(\text{NO}_3)_2$ is a hexagonal bipyramid (coordination number is eight), with two oxo-ligands in axial positions and six oxygen atoms of the $\text{C}=\text{N}^+-\text{O}^-$ and nitrate groups in the equatorial plane (Fig. 4). The uranyl group is linear with normal average $\text{U}-\text{O}(2)$ length of $1.74(1) \text{ } \text{Å}$ and an angle of 179.99° . As can be seen from Fig. 4, ligand exists in the trans-form and coordinates via the oxygen atom of nitrone group ($\text{U}-\text{O} \text{ } 2.361(11) \text{ } \text{Å}$). The coordinated ligand demonstrates a nitrone $\text{N}-\text{O}$ bond length of $1.334(14) \text{ } \text{Å}$ and $\text{C}=\text{N}$ length of $1.265(18) \text{ } \text{Å}$. The C-phenyl ring is twisted 8.2° from the nitrone plane and 103.9° from the equatorial plane of complex.

The planar four-membered metallacycle $\text{UO}(3)\text{N}(2)\text{O}(4)$ is characterized by an average UON angle of 97.2° and an average bond length $\text{U}-\text{O}$ of $2.532 \text{ } \text{Å}$. The nitrate groups have a practically planar quasi-triangular structure with an endocyclic angle $\text{O}(4)\text{N}(2)\text{O}(3) = 115.9^\circ$ and exocyclic angles of ca.

122.3° . The nitrate group is slightly distorted due to the coordination with $\text{N}(2)-\text{O}(3) = 1.239 \text{ } \text{Å}$ and $\text{N}(2)-\text{O}(4) = 1.272 \text{ } \text{Å}$, but $\text{N}(2)-\text{O}(5) = 1.213 \text{ } \text{Å}$.

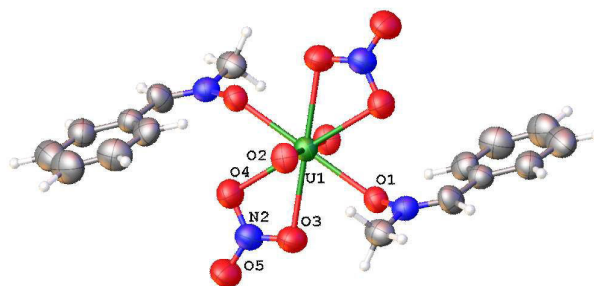


Fig. 4. Molecular structure of 4

Conclusions

The coordination behavior of α -phenyl-N-methylnitrone was studied. The new coordination compounds of copper, manganese, nickel and uranyl were characterized by IR and UV-Vis spectroscopies. Based on NMR spectroscopy data in the temperature range of 203–293 K, a dynamic process was proposed for the uranyl complex in acetone solution. The crystal and molecular structure of uranyl complex with α -phenyl-N-methylnitrone was determined by X-ray diffraction study. The monodentate nitrone ligands are coordinated to the metal ion via oxygen atom. The coordination polyhedron of uranium is a distorted hexagonal bipyramid.

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БУДОВА ТА СПЕКТРОСКОПІЧНА ХАРАКТЕРИСТИКА КООРДИНАЦІЙНИХ СПОЛУК З α -ФЕНІЛ-N-МЕТИЛНІТРОНОМ В РОЗЧИНІ ТА ТВЕРДОМУ СТАНІ

I.V. Raspertova, D.M. Khomenko, Z.D. Uzakbergenova, P.O. Doroshchuk, R.D. Lampeka

В даній роботі синтезовано нові координаційні сполуки міді(II), мангану(II), нікелю(II) та ураніл-іону з α -феніл-N-метилнітроном. Комплекси охарактеризовано за допомогою ІЧ, ЯМР та електронної спектроскопії. За допомогою рентгеноструктурного аналізу встановлено будову уранільного комплексу з α -феніл-N-метилнітроном. В екваторіальній площині два ліганди координуються через атом кисню. Решта чотири місця зайняті двома нітратними групами, координованими бідентатно. Координаційний поліедр урану – викривлена гексагональна біпіраміда. Для комплексу уранілу показано, що в діапазоні температур 203–297 К в ацетоновому розчині відбувається динамічний процес. Ядерний ефект Оверхаузера спостерігається між азометиновими та метильними протонами для двох присутніх форм органічного ліганду. Ліганд знаходиться у вигляді *транс*-ізомеру. Шляхом перекристалізації комплексу міді(II) з α -феніл-N-метилнітроном було одержано димерний бензоат міді(II). За даними рентгеноструктурного аналізу кожен атом міді має октаедричне оточення. Координаційна сфера сформована шістьма атомами кисню. Три аніони бензойної кислоти координовані бідентатно-містково через атоми кисню карбоксильних груп, одна молекула бензойної кислоти – монодентатно через кисень карбоксилу.

Ключові слова: нітрон, координаційні сполуки, ураніл, кристалічна будова, ЯМР-спектроскопія.

THE STRUCTURE AND SPECTROSCOPIC CHARACTERIZATION OF COORDINATION COMPOUNDS WITH α -PHENYL-N-METHYLNITRON IN SOLUTION AND IN SOLID STATE

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Keywords: nitron; complex; uranyl; crystal structure; NMR spectroscopy.

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