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Gulyaev Vitaliy, Doctor of technical sciences, Professor of the Department of Chemical and Biological Technologies

Kovalenko Alla, Candidate of chemical sciences, Associate Professor of the Department of Chemical and Biological Technologies

Yelatontsev Dmytro, Candidate of technical sciences, Associate Professor of the Department of Chemical and Biological Technologies

Filimonenko Olga, Senior lecturer of the Department of Chemical and Biological Technologies Dniprovsky State Technical University, Kamianske

Гуляєв В.М., д.т.н., професор, ORCID: 0000-0002-4991-6250, e-mail: vgulyaev@dnepro.net **Коваленко А.Л.**, к.х.н., доцент, ORCID: 0000-0003-1496-6634,

e-mail: ddtu.kafpbt@ukr.net

Єлатонцев Д.О., к.т.н., доцент, ORCID: 0000-0003-1043-418X, e-mail: sauron11652@gmail.com **Філімоненко О.Ю.**, старший викладач, ORCID: 0000-0001-9343-960X,

e-mail: olga.filimonenko82@gmail.com

Дніпровський державний технічний університет, м. Кам'янське

NOVEL COPPER(II) CHELATE COMPLEX WITH TRIS-(HYDROXYMETHYL)-AMINOMETHANE: STRUCTURAL CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY

The chelate complex $[Cu(TRIS-H)_2]\cdot 5H_2O$ was obtained and its elemental analysis, solubility, pH, and electrical conductivity were determined. The compound was studied by electronic and infrared spectroscopy, differential thermal analysis, electron paramagnetic resonance, and magnetochemistry. The total results of the compound analysis indicate that it is likely to be a monomer. Laboratory data indicate that the compound has antimicrobial and wound-healing properties, reduces the wound-healing time of postoperative patients, and can be recommended as a therapeutic drug.

Keywords: copper(II) complexes; amino alcohols; TRIS; electron paramagnetic resonance analysis; antimicrobial activity.

Одержано комплексну сполуку $[Cu(TRIS-H)_2] \cdot 5H_2O$ визначено її елементний аналіз, розчинність, pH, електропровідність. Сполука досліджена методами електронної та IV-спектроскопії, диференціального термічного аналізу, електронного парамагнітного резонансу, магнетохімії. Сукупність результатів аналізу сполуки свідчить що вона ймовірно являє собою мономер. Лабораторні дані свідчать про те що сполука володіє антимікробними та ранозагоювальними властивостями, скорочує термін загоювання ран післяопераційних хворих і може бути рекомендована як лікувальний препарат.

Ключові слова: комплекси міді(II); аміноспирти; TPIC; аналіз електронного парамагнітного резонансу; антимікробна активність.

Problem's formulation

There are several studies on the complexation of transition metals with tris-(hydroxymethyl)-aminomethane (TRIS) [1—6]. The interest in TRIS is caused by the fact that it has acid-base and reducing properties [7], can be a one-, two-, or three-dentate ligand, performs a chelate function, is a bridge between atoms of the same element or between atoms of different metals (heteronuclear complexes). TRIS interacts with transition metal ions, usually by deprotonating one of the OH groups [8].

Analysis of recent research and publications

In [9] cobalt(III) complexes with aminoisobutylglycerol type $Me\{Co[NH_2C(CH_2O)_2(CH_2OH)]_2\}\cdot nH_2O$ where Me is Na (n=5) or K (n=4) were described and

conclusions about their possible configuration were obtained from the data of electronic spectra compared to the similar complexes of diamine series $\text{Co}^{3+}\text{N}_2\text{O}_4$. It was of interest to obtain and study the physicochemical properties of complexes such as $[\text{Cu}(\text{TRIS-H})_2] \cdot \text{nH}_2\text{O}$.

When aqueous solutions of copper(II) salts interact with TRIS in an alkaline medium at pH ~10, the formation of an intra-complex compound (ICC) [Cu(TRIS-H)₂]·5H₂O occurs. The highest yield of the complex is achieved by taking an aqueous solution of copper acetate with TRIS in a ratio of 1:3.5. A slightly lower yield of DCS is obtained by the interaction of CuSO₄·5H₂O salt with TRIS in the alkaline medium in the ratio of 1:3.5 [10].

Not only copper(II) salts but also copper(II) bis-chelates with TRIS can be used as starting compounds [11]. The interaction of various copper(II) chelates with TRIS, such as $[Cu(TRIS-H)H_2O]-CI-H_2O$ or $[Cu(TRIS)_2]\cdot SO_4$ with a saturated aqueous alkali solution yields $[Cu(TRIS-H)_2]\cdot 5H_2O$ [12]. When attempting to obtain mixed complexes of copper(II) with N-derivatives of diethanolamine (DEA) such as RDEA, where R is C_3H_5 , C_5H_7 or C_4H_7 with TRIS in aqueous and alcoholic medium, only $[Cu(TRIS-H)_2]\cdot 5H_2O$ is obtained, which indicates fairly high stability of this complex [13].

Formulation of the study purpose

The study aims to synthesize a complex compound $[Cu(TRIS-H)_2] \cdot 5H_2O$ and determine its elemental composition, solubility, pH, and electrical conductivity. To perform physicochemical studies, obtain electronic and infrared spectra, perform differential thermal analysis, study electron paramagnetic resonance, and conduct magneto-chemical studies to determine the structure of the compound. Test the therapeutic properties of the synthesized compound in the healing of purulent wounds.

Presenting main material

In this study the compound [Cu(TRIS-H)₂]·5H₂O was prepared in several ways:

- (a) 1.70 g (0.01 mol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ salt in 2 cm³ water is treated with 2.42 g (0.02 mol) of TRIS and 1.60 g (0.04 mol) of caustic soda in 2 cm³ water. The mixture is filtered off. After 1 h a stick-shaped red-purple finely crystalline substance is formed. It is consequently successively washed with 1 mol dm⁻³ NaOH solution, ethanol, and ether, and dried in the air. Elemental analysis for $\text{CuC}_8\text{H}_2\text{ON}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$:
 - calculated, %: Cu 16.14; C 24.40; H 5.12; N 7.11.
 - found, %: Cu 16.15; C 24.40; H 5.13; N 7.10.

Melting temperature = 225—227 °C. The yield is 70 %.

- (b) Interaction of the $[Cu(CH_3COO)_2] \cdot H_2O$ salt with TRIS in the ratio 1:3.5 in aqueous medium. Found, %: Cu 16.14; C 24.39; H 5.15; N 7.10. The yield is 75 %.
- (c) Interaction of $CuSO_4\cdot 5H_2O$ salt with TRIS and caustic soda in the ratio 1:3.5:3. Found, %: Cu-16.14; C-24.42; H-5.11; N-7.10. The yield is 65 %.
- (d) 0.93 g (0.0025 mol) of the complex [Cu(TRIS₂-H)H₂O]·Cl·H₂O in 2.5 cm³ of water is treated with a solution of 0.40 g (0.001 mol) of caustic soda in 2 cm³ water. Found, %: Cu 16.13; C 24.40; H 5.13; N 7.11. The yield is 65 %.
- (e) 1.0 g (0.0025 mol) of $[Cu(TRIS)_2] \cdot SO_4$ chelate is dissolved in 3 cm³ water and treated with a solution of 0.50 g (0.0125 mol) of caustic soda in 3 cm³ of water. Found, %: Cu 16.17; C 24.40; H 5.15; N 7.10. The yield is 55 %.
- (f) By heating on a water bath the chelate [Cu(TRIS₂-H)H₂O]·Cl·H₂O with N-derivatives of diethanolamine type (R-DEA), where R is C_3H_5 , C_5H_7 or C_4H_7 in the ratio 1:3. Found, %: Cu 16.14; C 24.42; H 5.12; N 7.11. The yield is 50 %.
- (g) 0.005 mol of bis-chelate $[Cu(RDEA-H)Cl]_2 \cdot nH_2O$, where R is C_3H_5 , C_5H_7 or C_4H_7 in 8 cm³ of methanol treated with 0.001 mole of TRIS. Found, %: Cu 16.13; C 24.40; H 5.11; N 7.11. The yield is 50 %.

Copper(II) in the complexes was analyzed by the iodometric method [14]. The content of carbon, hydrogen, and nitrogen was determined on C, H, and N analyzers by Hewlett-Packard Model 185.

Electronic absorption spectra of complexes in the solid state were recorded on Shimadzu UV-3101 PC spectrophotometer (Japan); in solution — on microcomputer double-beam spectrophotometer SPECORD M 40 (Carl Zeiss Jena).

IR spectra of the substance were recorded on a Perkin-Elmer 325 spectrophotometer in the region of 200—4000 cm⁻¹. The complexes were suspended in fluorinated and vaseline oils. Thermal

studies of the complexes (DTA) were performed on the derivatograph system Paulik-Paulik-Erdei in the range of $30-500^{\circ}$ in the atmosphere of air. Samples (50-100 mg) were heated in a platinum crucible at a rate of 5° per minute.

EPR spectra were recorded on an X-band radio-spectrometer RE-1307 (v = 9 GHz) in the temperature range 98–300 K. Determination of the g-tensor and calculation of the EPR spectra parameters were performed according to [15].

The Faraday method; Co[Hg(CNS)4] determined the complexes' magnetic susceptibility.

Complex [Cu(TRIS-H)₂]·5H₂O in the individual state is a fine crystalline substance of redviolet color, well soluble in alkaline solutions, weakly soluble in water and organic solvents – dimethylformamide (DMFA), dimethylsulfoxide (DMSO), in strongly acidic solutions the complex is destroyed. In air the substance gradually changes, especially under the influence of water vapor, its redviolet coloring turns to blue [16].

Qualitative reactions indicate the absence of sodium cations as well as Cl⁻, SO₄²⁻, COO⁻ anions in aqueous solutions of the complex, which excludes the presence of [Cu(TRIS₂-H)H₂O]·Cl·H₂O, [Cu(TRIS)₂]·SO₄ complexes as impurities.

Compound [Cu(TRIS-H)₂]· $5H_2O$ practically does not dissociate into ions and is a representative of nonelectrolytes. The molar electric conductivity of a millimolar aqueous solution of [Cu(TRIS-H)₂]· $5H_2O$ complex at 20 °C is ~14 Ohm⁻¹ cm² mol⁻¹. This indicates a partial protonation of ICC in aqueous medium. The pH of this solution is 9.45 and practically does not change in time.

In the solid state, the absorption spectrum of [Cu(TRIS-H)₂]·5H₂O is characterized by an asymmetric broad band with weak splitting with a maximum at 17200 cm⁻¹ (Fig. 1).

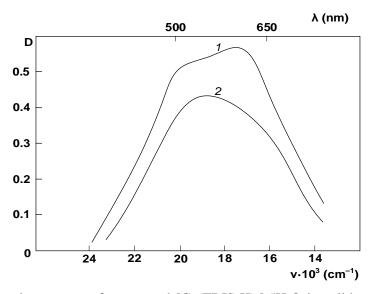


Fig. 1. Absorption spectra of compound [Cu(TRIS-H)₂]·5H₂O in solid state (1) and in 1 M NaOH (2) after 3 minutes after the preparation of solution (l = 1 cm, c = 0.01 mol dm⁻³)

The spectrum of the compound in 1 mol dm⁻³ solution of caustic soda is similar to the spectrum of an individual complex and contains a broad asymmetric absorption band with a barycenter at ~17000 cm⁻¹ (Fig. 1). The absorption spectrum practically does not change with time, which testifies to sufficient stability of the compound in these conditions.

Tabl. 1 presents the values of frequencies observed in the IR spectra of the [Cu(TRIS-H)₂]· $5H_2O$ complex. The ligand molecule contains an NH₂-group and three hydroxyl groups which are absorbed in the region of 3100—3600 cm⁻¹ in the IR spectrum.

The absorption bands with a maximum at $3400-3300 \text{ cm}^{-1}$ should be attributed to vibrations of the OH group and the bands at $3250-3155 \text{ cm}^{-1}$ to absorption of the NH₂ group. Such relatively low frequencies v(NH) and v(OH) indicate the presence of intramolecular hydrogen bonds.

Table 1. Vibrational frequencies (cm $^{-1}$) found in the IR spectra of TRIS and it's complex [Cu(TRIS-H)₂]·5H₂O

| Vibration | Compound | | | |
|---|--|------|---|------|
| | NH ₂ C(CH ₂ OH) ₃ | | [Cu(TRIS-H) ₂]··5H ₂ O | |
| ν(ΟΗ) | 3400 | 3300 | 3400 | 3520 |
| ν(NH) | 3250 | 3155 | 3260 | 3200 |
| $\delta(NH_2)$ | 1630 | 1605 | 1560 | 1625 |
| δ(CCH) δ(NCH) δ(CH ₂) | 1510 | 1455 | 1460 | 1495 |
| $\nu(CN)$ $\delta(CH_2)$ | 1450 | - | 1430 | 1450 |
| δ(NH ₂) δ(COH) | 1380 | 1345 | 1380 | 1390 |
| δ(CCH) δ(NCH) | 1318 | 1293 | 1310 | 1335 |
| δ(CCH) δ(OH) | 1245 | 1230 | 1275 | 1245 |
| v(CN) | 1110 | - | 1160 | 1087 |
| v(CC) | 1067 | - | 1077 | 1055 |
| v(CO) | 1018 | - | 1025 | - |
| ν(CN) ρ(CH) | 947 | 903 | 950 | - |
| ν(CC) ρ(CH) | - | - | 925 | 910 |
| ν(CO) ρ(CH) | 835 | - | 870 | 830 |
| β(CH) γ(OH) | 725 | - | 780 | 750 |
| ν(Cu-O) ν(CC) | 600 | - | 670 | 640 |
| v(Cu-N) | - | - | 570 | 510 |
| ν(Cu-N) γ(CNC) | 427 | - | 460 | 400 |
| ν(Cu-O) δ(O-CuO) | - | - | 380 | 345 |
| ν(Cu-N) δ(N-CuN) | - | - | 300 | 265 |

In the 1600—1650 cm⁻¹ interval, two absorption bands with maximums at 1630 and 1605 cm⁻¹ are observed in the TRIS spectrum. The high-frequency band apparently should be attributed to the strain asymmetric vibration of $\delta_{as}(NH_2)$ amino groups, and the low-frequency band to the asymmetric vibration of $\delta_{as}(OH)$ groups. The absorption bands of the symmetric vibrations $\delta_s(NH_2)$ and $\delta_s(OH)$ are observed at 1380 cm⁻¹ and 1345 cm⁻¹, respectively.

The δ (CCH), δ (CH2), and δ (NCH) vibrations are evident at 1510, 1455, 1318, and 1293 cm⁻¹. Absorption of C–N valent vibrations is observed at 1160, 1100, 987, and 947 cm⁻¹, of C–C valent vibrations at 1065, 1045, and 903 cm⁻¹, and absorption of C–O valent vibrations is manifested by bands

with maximums at 1032, 1018, 860, and 835 cm⁻¹. In the region below 700 cm⁻¹, the absorption bands $\nu(CC)$, $\nu(CCN)$, and $\gamma(CCNC)$ are observed at 680, 600, 450, and 427 cm⁻¹, respectively.

In the IR spectrum of the $[Cu(TRIS-H)_2]-5H_2O$ complex, a series of absorption bands are observed in the absorption region of NH_2 and OH-groups, some of which refer to bound NH_2 and OH-groups. The high-frequency band with a maximum at 3400 cm⁻¹ apparently can be attributed to a free OH-group bound by hydrogen bonds with crystallization water molecules or participating in some other interaction.

The absorption bands $\delta(NH_2)$ and $\delta(OH)$ undergo a low-frequency decrease (by ~30 cm⁻¹ and ~15 cm⁻¹, respectively), which indicates the coordination of NH_2 and OH groups. Coordination through the nitrogen atom is confirmed by the shift in the absorption bands $\delta(NCH)$, $\delta_{as}(NH_2)$, $\nu(C-N)$, etc. (Tabl. 1).

Absorption bands appear in the region of $500-600 \text{ cm}^{-1}$, $400-460 \text{ cm}^{-1}$, and $250-300 \text{ cm}^{-1}$ in the IR spectrum of [Cu(TRIS-H)₂]·5H₂O, some of which can be attributed to (Cu–N) vibrations. The formation of (Cu–O) bonds leads to changes in the frequencies δ (OH) and ν (C–O) in addition to the low-frequency shift of the ν (OH) frequencies. In the absorption region of ν (Cu–O), absorption bands with a maximum at 675, 605, 375, and 350 cm⁻¹ are observed.

Derivatograms of the complex testify to the fact that upon heating of the compound in the temperature range of 50—60, °C water weakly bound with hydrogen bonds is detached (found mass loss of 7 %, i.e. 1.5 water molecules), up to 80 °C, 3 more water molecules are detached (mass loss of 15%). When heated to a higher temperature in the 130—150 °C range, the remaining water is lost and the amino alcohol begins to detach.

Table 2. Temperature dependence of magnetic moment of compound [Cu(TRIS-H)₂]·5H₂O

| T (K) | Magnetic moment (μ _B) |
|-------|-----------------------------------|
| 299 | 1,91 |
| 213 | 1,90 |
| 176,6 | 1,88 |
| 153 | 1,91 |
| 127 | 1,90 |
| 81,5 | 1,90 |

Tabl. 2 shows the temperature dependence of the magnetic moment of the compound [Cu(TRIS-H)₂]·5H₂O.

In the temperature range of 80—300 K, the magnetic moment value of the complex practically does not change and corresponds to the monomeric compound with $S=\frac{1}{2}$.

Fig. 2 shows the EPR spectrum of the compound $[Cu(TRIS-H)_2] \cdot 5H_2O$.

The shape of the line of the EPR spectrum (Fig. 2) of the complex [Cu(TRIS-H)₂]·5H₂O is an asymmetrical singlet and is typical for magnetically concentrated monomeric Cu(II) compounds with axial g-factor anisotropy (g₁ = 2,068, $\Delta H = 100$ Oe – at 300 K; g₁ = 2,066, $\Delta H = 90$ Oe – at 103 K) [17]. The line width does not change significantly with decreasing temperature, indicating that the main factor broadening the individual line is the dipole-dipole spin-spin interaction between the copper ions.

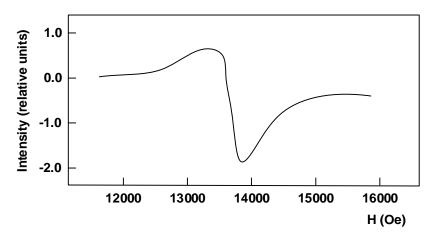


Fig. 2. EPR spectrum of the compound [Cu(TRIS-H)₂]·5H₂O

The combination of physical and chemical analysis data indicates that the complex $[Cu(TRIS-H)_2]\cdot 5H_2O$ has a distorted or square-planar configuration, the deprotonated ligand is attached to the central ion of N,O or N,O,O' type, water molecules are linked by hydrogen bonds with the free group OH and with the oxygen atom of the ligand oxy-groups.

The complex has a trans-structure as evidenced by the absorption bands at 1560, 1380, 1365, 1275 and 1018 cm⁻¹. The structure of the complex can be represented by the following formulas (Fig. 3):

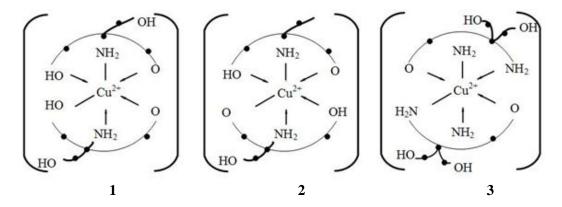


Fig. 3. Possible structures of the studied compound

The X-ray studies [18] of the [Cu(TRIS-H)₂]·5H₂O complex showed that model 3 actually exists. The antibacterial properties of this compound as a prophylactic and therapeutic agent in purulent-inflammatory complications were studied on strains of microorganisms, including carriers of *Escherichia coli* and *Pseudomonas aeruginosa*, *Enterobacter*, *Proteus*, *Coccus flora*, etc. 108 strains of microorganisms were isolated from purulent wounds of surgical and urological patients and microbiological studies were performed with them [19]. A serviette, which is a dressing material based on gauze or cotton textile, was immobilized with complex [Cu(TRIS-H)₂]·5H₂O and was used on 45 white rats of *Vistar* line for treatment of simulated purulent "surgical" and "urological" wounds using the flora of patients. The results of the in vitro microbiological studies permit us to conclude the presence of a pronounced antimicrobial action of the proposed wipes and to establish the minimum inhibitory concentration (MIC), which is 8000 μg cm⁻³, and the conducted series of experiments on rats confirm the presence of pronounced antimicrobial properties of the wipes, with the wound healing time in animals being shortened by 5—7 days.

Comparing the results of treatment of wounds similar to those in surgical patients and treatment of wounds in animals with the "urological" wound model, no special differences in the duration of the wound process were noted, which allows us to say that the wipes with metal complex have an equally good antibacterial effect in both cases.

Thus, carried out research showed the presence of an antimicrobial effect that makes it possible to implement them for the treatment of wounds in urological patients after operations of adenomectobolony, resection of the bladder with a tumor, cystostomy, and also in surgical patients with suppuration of postoperative wounds after the opening of tendon panaritis, purulent mastitis, suppuration of a cut wound in the stomach, soft tissue wounds of the femur, trophic ulcers.

Morphological changes in the wounds of 21 patients with purulent-inflammatory complications of soft tissues in the course of their local treatment with napkins with immobilized metal complex copper(II) and traditional preparations were studied [20]. A more effective impact of the proposed tissues compared to the traditional preparations for the local treatment of purulent-inflammatory complications in wounds on their repair processes in surgical and urological patients was proved.

Application of the suggested napkins for local treatment of purulent-inflammatory complications in the wounds of the patients after surgical and urological operations accelerates the formation of granulations in them, clearing of the necrotic tissues, the appearance of the edge epithelization which is proved by the performed histological and cytological studies. Final wound healing is reduced by an average of 9 days compared to traditional means of local treatment, which allows for significantly reduced treatment of patients.

Conclusions

- 1. Thus, based on electron, IR spectroscopy, EPR, DTA, and magnetic susceptibility data, we can assume that the resulting compound has a monomeric centrosymmetric structure with a transconfiguration. There is no electron-exchange interaction, the TRIS ligand acts as a single-charged anion and forms five-membered cycles with a Gauche conformation.
- 2. The results of the in vitro microbiological studies permit us to conclude that the wipes containing a metal complex of copper(II) with TRIS have a strong antimicrobial action and a MIC of 8000 μ g cm⁻³, while the wound healing time in animals was reduced by 5—7 days.
- 3. Morphological changes in postoperative patients with purulent-inflammatory complications due to the application of a napkin with the immobilized complex compound of copper(II) and traditional preparations for local wound treatment were studied. It has been established that the duration of tissue regeneration in purulent wounds of patients who have applied napkins with $[Cu(TRIS-H)_2] \cdot 5H_2O$ is reduced by an average of 9 days compared to traditional treatment methods.

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НОВА ВНУТРІШНЬОКОМПЛЕКСНА СПОЛУКА МІДІ(ІІ) З ТРИС-(ОКСИМЕТИЛ)-АМІНОМЕТАНОМ: СТРУКТУРА ТА АНТИБАКТЕРІАЛЬНІ ВЛАСТИВОСТІ

Реферат

Синтезований комплекс міді(II) з аміноізобутилгліцерином — трис-(оксиметил)-амінометаном, (NH₂C(CH₂OH)₃, — (TPIC) — [Cu(TPIC-H)₂]·5H₂O. Склад сполуки досліджений методами електронної та IЧ-спектроскопії, диференціального термічного аналізу (ДТА), електронного парамагнітного резонансу (ЕПР) та магнітної сприйнятливості. В ІЧ-спектрі комплексу відзначені смуги поглинання в області 3400 см⁻¹, віднесені до коливань вільної ОН-групи; смуги в області 500—600, 400—460, 250—300 см⁻¹ — до коливань v(Cu–N); 675, 605, 375, 350 см⁻¹ — до коливань v(Cu–O). Ефективний магнітний момент[Cu(TPIC-H)₂]·5H₂O в інтервалі 80-300 К дорівнює 1,91 μ B. Форма лінії спектру ЕПР комплексу [Cu(TPIC-H)₂]·5H₂O типова для магнітоконцентрованих мономерних сполук міді з аксіальною анізотропією g-фактору ($g_1 = 2,068$ — при 300 K; $g_1 = 2,066$ — при 103 K). Висловлено припущення про мономерну будову комплексу, ліганд приєднується до центрального іону у вигляді атомів азоту та кисню. На підставі даних електронної та ІЧ-спектроскопії, магнітної сприйнятливості, ДТА та ЕПР висловлено припущення про моноядерну будову комплексу.

Отримана сполука має виражені антимікробні та ранозагоювальні властивості. Застосування запропонованих серветок для місцевого лікування гнійно-запальних ускладнень у ранах хворих після хірургічних та урологічних операцій сприяє прискоренню утворення в них грануляцій, очищенню некротизованих тканин, появі крайової епітелізації, про що свідчать проведені гістологічні та цитологічні дослідження. Отримана сполука скорочує час загоєння ран порівняно з традиційними методами лікування в 1,5—2,0 рази.

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