ISSN 1027-5495. Functional Materials, 30, No.1 (2023), p. 120-127.
doi:https://doi.org/10.15407/fm30.01.120

Guanidinium-containing oligoether as a complexing agent of transition metal ions

***M.Ya.Vortman*[1], *O.S.Berezhnytska*[3], *O.A.Aksenovska*[2], *S.M.Kobylinskyi*[1], *L.V.Kobrina*[1], *V.N.Lemeshko*[1], *V.V.Shevchenko*[1]**

[1]Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 48 Kharkiv Highway, 02160 Kyiv, Ukraine
[2]V.P.Kukhar Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, 50 Kharkiv Highway, 02160 Kyiv, Ukraine
[3]V.I.Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, 32/34 Palladin Ave., Kyiv, Ukraine

Received September 1, 2022

Metal complexes based on guanidinium-containing oligoether and Cu^{2+}, Ni^{2+}, Co^{2+} or UO_2^{2+} ions have been synthesized. The structure of the initial ligand and obtained complexes, as well as the complexing ability of the oligoether towards the transition metal and radionuclide ions was investigated by FTIR, NMR and UV-Vis spectroscopy. It is shown that the synthesized oligomer forms stable complexes with the ions under study. Their coordination number is 6 and the resulting complexes have the form of a distorted octahedron. The chemical composition of the complexes in solution and in the solid state did not change.

Keywords: guanidinium-containing oligoether, complexation, FTIR and UV-Vis spectroscopy.

Гуанідинвмісний олігоетер як комплексоутворювач іонів перехідних металів. *М.Я.Вортман, А.С.Бережницька, О.А.Аксеновська, С.М.Кобилінський, Л.В.Кобріна, В.М.Лемешко, В.В.Шевченко*

Синтезовано металокомплекс на основі гуанідинійвмісного олігоетеру і солей полівалентних металів Cu^{2+}, Ni^{2+}, Co^{2+} та UO_2^{2+}. Методом ІЧ, ЯМР та електронної спектроскопії досліджено структуру вихідного ліганду та отриманих комплексів та комплексоутворювальну здатність олігоетеру стосовно іонів полівалентних металів Cu^{2+}, Ni^{2+}, Co^{2+} та UO_2^{2+}. Показано, що синтезований олігомер утворює стійкі комплекси з іонами полівалентних металів; координаційне число комплексів дорівнює 6, отримані комплекси мають форму деформованого октаєдра. Встановлено незмінність хімічного складу комплексів у розчині та в конденсованому стані.

1. Introduction

One of the main problems that arise during wastewater treatment of various industries is the removal of transition metal ions from aqueous solutions. The solution to this problem is possible by using compounds capable of forming stable complexes with metal ions [1–4].

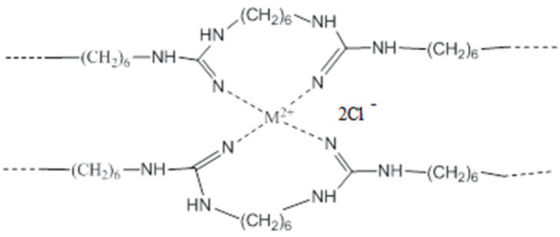
Guanidine and its derivatives are of interest as ligands in coordination chemistry due to the presence of the CN_3 fragment; they are also good electron donors due to the delocalization of six π-electrons in the Y-shaped part of the CN_3 fragment, which is called Y-aromaticity [5] or resonance stabilization and is the main reason for the

high basicity of guanidines. This makes them versatile and efficient ligands for transition metal ions such as Mn, Co, Ni, Zn, Cd, Hg and Ag [5–7].

The first complexes were described for 1,1,3,3-tetramethylguanidine (TMG) with Co^{2+} and Cu^{2+} ions. The compositions of these complexes are as follows $[Co((CH_3)_2NC{:}NHN(CH_3)_2)_4](ClO_4)_2$, $[Cu((CH_3)_2NC{:}NHN(CH_3)_2)_4](ClO_4)_2$ that indicates the complexation of four TMG molecules with one metal ion. Bisguanidines are characterized by the formation of complexes with the M:L ratio of 1:1 — $[M(L)Y_2]$, where MY_2 is metal salt, L is ligand — bisguanidine. The structure of these complexes is basically a distorted tetrahedron. [8, 9], and they are used in various fields of bioorganic chemistry, as well as polymerization catalysts. Peralkylated and bicyclic guanidines coordinated with transition metals have been also described. Guanidinocarbon ligands are widely used in coordination and organic chemistry as pharmaceuticals, sweeteners, catalysts [8, 9].

Among polymeric complexing agents, polyethyleneimine is one of the most widely used ligands due to the presence in its structure of a large number of amine groups capable of protonation and complexation [10–16]. However, the most demanded in terms of practical use are polymeric guanidine derivatives, for example, polyhexamethylene guanidine chloride (PHMGC), which attract attention due to their biocidal properties [17–19]. The PHMGC mechanism of binding metal ions may be as follows: similar to polyethylenimine, polyhexamethylene guanidine chloride and phosphate (PHMGF) form complex compounds with metal ions. This makes it possible to consider PHMGC as a promising platform for chelate complex formation with the target metal ion.

The metal ions in these complexes are quite strongly bound to polyhexamethylene guanidine chains and they cannot be replaced by other cations. The assessment of stability constants by the Bjerrum method [17–19] allows us to arrange them in the following order: $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Pb^{2+} > Hg^{2+} > Mn^{2+}$



A characteristic feature of PHMGF complexes is the closeness of all consecutive constants of the complex formation. It is due to the high local ligand concentration of PHMGF macromolecules, which coagulated into static tangles, as well as with the fact that all ligands are bound together by the valence chain of the polymer molecule. The latter circumstance leads to the fact that the addition of the first elementary link immediately forms a complex with four ligands.

Polyhexamethylenguanidinium chloride and phosphate are formed stable complexes with heavy metal ions in aqueous solutions; this leads to displacing a proton from the protonated imine group of the polymer. The complexing ability of PHMG depends on the nature of the metal and the concentration of the polymer in the solution. Binding of metal ions occurs inside the statistical macromolecular tangles of the polymer. The most complete interaction occurs in dilute solutions at a concentration of PHMG up to 3 %. Due to the polyelectrolyte effect in this concentration range, macromolecular tangles are maximally unfolded, which facilitates complex formation. In the complexes formed, one metal ion accounts for 10–16 elementary links of the polymer. Binding of metal ions into strong polymeric complexes with PHMGC is used for their removal from wastewater of industrial enterprises and the body of warm-blooded animals. The use of polyguanidines paved the way for their wider application in coordination chemistry.

It should also be noted that the chemistry of oligomeric guanidine derivatives opens wide possibilities for changing the structure and physicochemical properties of oligomers as ligands. In particular, a certain potential is inherent in providing such oligomers with amphiphilic properties.

Previously, we have obtained a guanidine-containing oligoether by the reaction of oligomeric aromatic diepoxide with guanidine, neutralized by hydrochloric acid [20], as well as some other organic and inorganic acids [21]. It should be noted the availability of raw materials and low energy consumption in the synthesis of the described oligomers. In this regard, it is reasonable to investigate guanidinium oligomeric complexes with transition metal ions.

The aim of this research is to synthesize metal complexes based on guanidinium-containing oligoether and copper (II), nickel (II), cobalt (II), uranyl (UO_2^{2+}) ions. Investigation of the obtained complexes by UV-Vis (liquid and solid states), FTIR, and NMR methods.

2. Experimental

Materials. DER-331 is a diane epoxy oligomer (MW 365 g/mol) diglycidyl ether of bisphenol A. The weight part of the epoxy groups is 23.5 wt.%. The DER-331 was dehydrated at temperature 80–90°C in vacuum (residual pressure of 2 mmHg) for 2–6 hours.

Guanidine hydrochloride (Aldrich) was used without additional purification.

Inorganic salts of copper(II) sulfate ($CuSO_4 \cdot 5H_2O$, 99 %) and nickel(II) sulfate ($NiSO_4 \cdot 6H_2O$, 99 %), cobalt (II) chloride ($CoCl_2 \cdot 6H_2O$, 99 %) and $UO_2(NO_3)_2 \cdot 6H_2O$ (pure for analysis grade) — all chemicals were used without additional purification.

Synthesis of guanidinium-containing oligoether (GO). The GO sample was synthesized according to the method described in [20]. Briefly, the synthesis of GO is based on the reaction of an epoxy oligomer and guanidine in the base form, obtained immediately before the reaction at a molar ratio of components 1:2. The synthesis of oligoether was carried out at 50 – 60°C for 2 – 3 h, followed by the treatment of the reaction mixture with hydrochloric acid to convert the product into a salt form. The resulting oligomer was isolated from the reaction mixture by precipitation in diethyl ether, and then dried at room temperature in vacuum to constant weight. The yield of the final product is 93 %. The obtained oligomer is a yellow resinous substance, soluble in water, ethanol, methyl ethyl ketone, dimethylformamide, dimethylsulfoxide, dimethylacetamide and insoluble in acetone, ethyl acetate, tetrahydrofuran, hexane.

Synthesis of Cu(II), Co(II) and Ni(II) complexes with guanidinium-containing oligoether. Complexes of metal ions (M(II)) with guanidinium-containing oligoether were obtained in an alcohol solution with a molar ratio L:M(II) = 2:1 at room temperature.

Complex of GO with Cu(II). A copper sulfate solution of 2.5 g (0.1 mol) in water/methanol 30/70 (v/v) was slowly added to 11.1 g (0.2 mol) of guanidinium-containing oligoether in a water/ethanol (50/50 (v/v)) solution with constant stirring. The resulting product was kept at room temperature for an hour and then dried at room temperature and reduced pressure. Precipitation of the complexes was carried out at pH 5.5 from the aqueous solution using a phosphate buffer solution (potassium dihydrophosphate). Then the obtained product was washed with ethanol and dried in a desiccator at room temperature in a vacuum to constant weight. The yield of the resulting product was 12.6 g (93 %). The obtained Cu(II) complex is a viscous resinous substance of green color. This complex is soluble in water, ethanol, methanol, dimethylformamide, dimethylacetamide.

The complexes of GO with Ni(II), Co(II) and UO_2^{2+} ions were obtained by a similar procedure with a molar ratio L:M = 2:1.

Characterization methods. The molecular weight of the ligand was determined using a Du Pont LC 8800 Size exclusion liquid chromatography kit with Zorbax PSM bimodal columns [20].

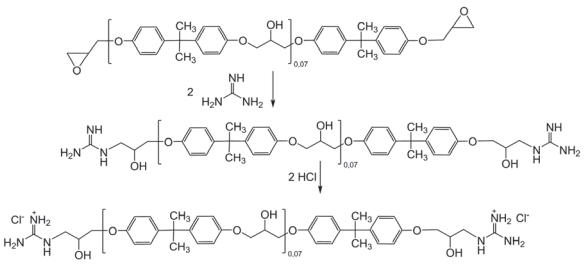
FTIR spectra of the ligands and the resulting metal complexes were recorded in the KBr tablet technique on a TENSOR 37 spectrophotometer in the region of 6000–400 cm^{-1}. ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-400 MHz device in $CDCl_3$.

The UV–Vis absorption and diffuse reflection spectra of the obtained complexes were obtained using spectrophotometer (UV-2401, Shimadzu) in the range of 50000–12000 cm^{-1}.

3. Results and discussion

The synthesis of guanidinium-containing oligoether ligand is presented in a follows schema [20]:

The chemical structure of the obtained oligomer was confirmed by various instrumental methods. In the IR spectrum of the oligomer (Fig. 1, curve 1) in the region of



3200–3550 cm^{-1}, there are absorption bands of valence vibrations of OH and NH groups. The IR spectrum of the ligand shows a band at 1655 cm^{-1} corresponding to the valence vibrations of the C=N bond. In the range of 1450 – 1650 cm^{-1} there are absorption bands of C–H bonds of a benzene

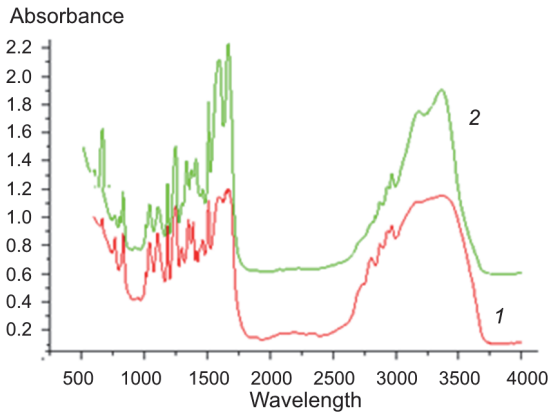


Fig. 1. FTIR absorption spectra of 1–GO and 2–Cu–GO complex.

ring. The presence of the OH group is also confirmed by bending vibrations at 1110 cm^{-1}. Compared to the initial products, the absorption bands of epoxy groups disappear at 920 cm^{-1}.

In the ^1H NMR ($CDCl_3$) spectrum of the ligand (Fig. 2a), there are signals of protons of methylene groups $NH–CH_2$ at 2.73 ppm and the signals of protons of oxirane cycle disappear. In the ^1H NMR spectrum there are also signals at 1.72 ppm. (*s*, 3H, $–CH_3$(a)), 2.73 ppm $–CH_2$ ($NH–CH_2$ (c)), 2.58 ppm $–CH_2$ (CH_2CHOH (b)), 3.58 ppm –OH (CH–OH (d)), 3.96 ppm –CH (CH–OH (e)), 6.8 ppm and 7.2 ppm –CH (f) benzene ring, 7.77 ppm, 8.4 ppm and 8.6 ppm –NH(NH) groups (f)).

In the ^{13}C NMR spectrum (Fig. 2b) of the ligand there are signals: 30.9 ppm. ($–CH_3$ (j)), 42.2 ppm, ($–C(CH_3)_2$, $–CH(NH–CH_2CHOH)$ (i)), 68.8 ppm (–CH(CHOH) (h)), 73.5 ppm ($–CH_2(O–CH_2CHOH)$ (h)), 114.9 ppm and 127.1 ppm (–CH aromatic ring (f) and (e)), 156 ppm (–CH–O aromatic ring (c)), 160 ppm (–C=N (b)).

The calculated average molecular weight of the ligand is 516 g/mol and is close to the theoretically calculated one (556 g/mol). The polydispersity coefficient of the synthesized ligand is 1.06, which indicates a narrow molecular weight distribution.

The content of copper, nickel and cobalt in the complex was determined by elemental analysis. Cu content: theory — 5.03 %, found — 4.85%, Ni content: theory — 4.39 %, found — 4.18 %, Co content: theory — 4.37 %,, found — 4.10 %. This made it possible to establish that the found value is close to the theoretically predicted calculated value at a molar ratio of oligomer: metal of 2:1. The formation of a complex is indicated by a change in color from blue to turquoise when a guanidinium-containing oligomer is complexed with cop-

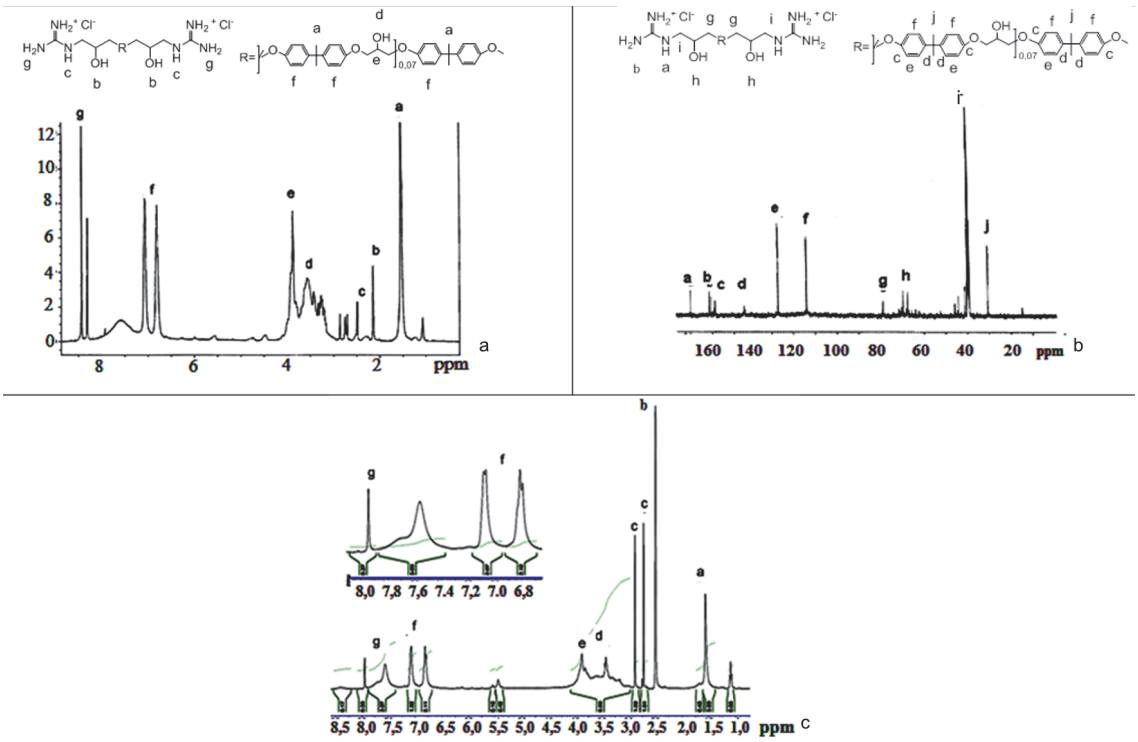


Fig. 2. ^1H (a) and ^{13}C (b) NMR spectra of GO c - ^1H NMR - spectrum of the complex Cu–GO

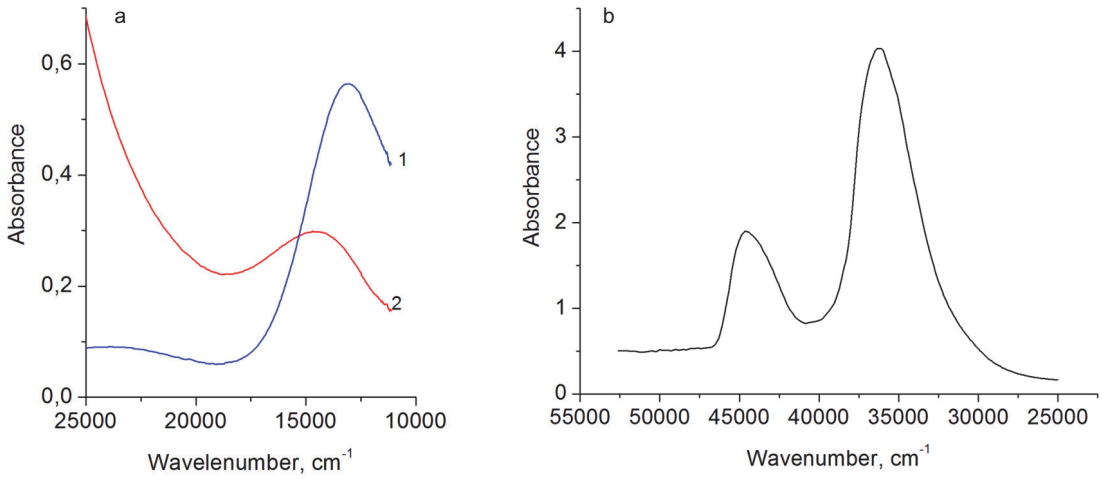


Fig. 3. UV spectra of copper sulfate (*1*) and complex Cu–GO_2 (*2*); (A) B-initial ligand.

per, from green to blue-violet with nickel and from pink to red maroon — with cobalt.

Thus, the metal ions in the synthesized complexes are in coordination with two oligomer molecules and are designated as M^{2+}–GO_2.

The structure of the obtained complexes was confirmed by IR, ^{1}H NMR and UV spectroscopy. The IR spectra of the synthesized complexes were analyzed by comparing with the spectrum of the original guanidinium-containing oligoether. The FTIR spectrum of the GO-Cu^{2+} complex shows (Fig. 1 curve 2) more intense valence vibrations of the NH group and OH groups. An increase in the intensity of the deformation bands of OH-groups and valence vibrations of the C=N bond was also observed, which may indicate the participation of amino and hydroxyl groups in the formation of donor-acceptor bonds with copper ions. The band at 632 cm^{-1} in the IR spectrum of the complex can be attributed to the valence vibrations of the M–N bond.

Table 1 shows the main characteristic bands of the FTIR spectra of GO complexes with transition metal and uranyl ions. As can be seen from these data, the M–N absorption band appears in all IR spectra of the complexes.

The ^{1}H NMR spectrum of the Cu^{2+}–GO complex (Fig. 2c) shows signals at 1.52 ppm. (–CH_3(a)), 2.73 ppm –NH(NHCH_2 (c)), 2.58 ppm –CH_2(CH_2CHOH (b)), 3.58 ppm –OH(CH–OH (d)), 3.96 ppm –CH(CH–OH (e)), 6.8 ppm and 7.1 ppm –CH (f) of the benzene ring, 7.6 and 7.95 ppm –NH(NH_2) group (f)). The data presented in Fig. 2c indicate a change in the intensity of the signals at 2.73 and 2.8 ppm –NH(NHCH_2 (c); also the signals –OH(CH–OH (d)), 3.96 ppm –CH (CH–OH (e)) are broadened, and the signals –NH (NH_2 groups (g)) 7.6 and 7.95 ppm are shifted. These data indirectly indicate that the amine and hydroxyl groups of the ligand are involved in the complex formation.

Since the formation of the M–N coordination bond can be confirmed by UV spectroscopy, electronic spectra are recorded for the synthesized compounds.

UV spectroscopy is traditionally used as a convenient method of establishing the symmetry of the nearest environment for most 3*d* metal ions, based on the analysis of the position and intensity of the absorption bands of *d*–*d* transitions. In the electronic

Table 1. The bands of FTIR spectra of GO and corresponding complexes with transition metals

Sample	ν(NH), cm^{-1}	δ(NH), cm^{-1}	ν(C=N), cm^{-1}	ν(CN), cm^{-1}	ν(OH), cm^{-1}	ν(M-N), cm^{-1}
GO	3430	1600	1632	1110	3338	–
Cu–GO	3420	1590	1655	1118	3488	632
Co–GO	3415	1590	1634	1049	3407	661
Ni–GO	3515	1580	1656	1028	3437	624
UO_2–GO	3450	1540	1650	910	1000	1050

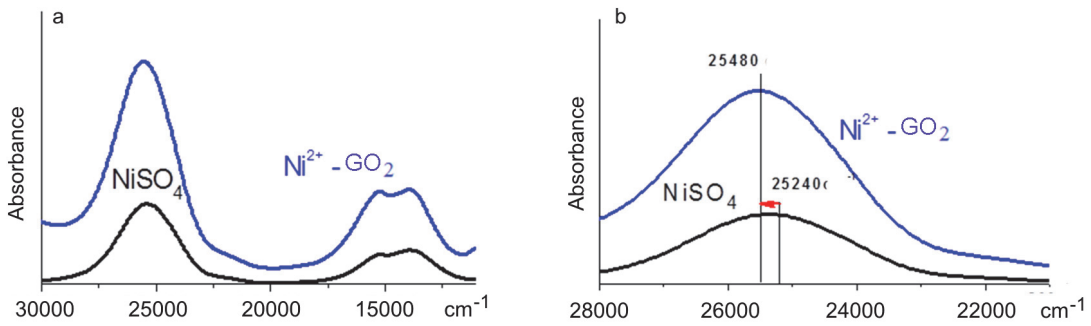


Fig. 4. UV spectra of $NiSO_4$ and Ni^{2+}–GO complex in the various ranges: 30000–12000 cm^{-1} (A) and 28000–20000 cm^{-1} (B).

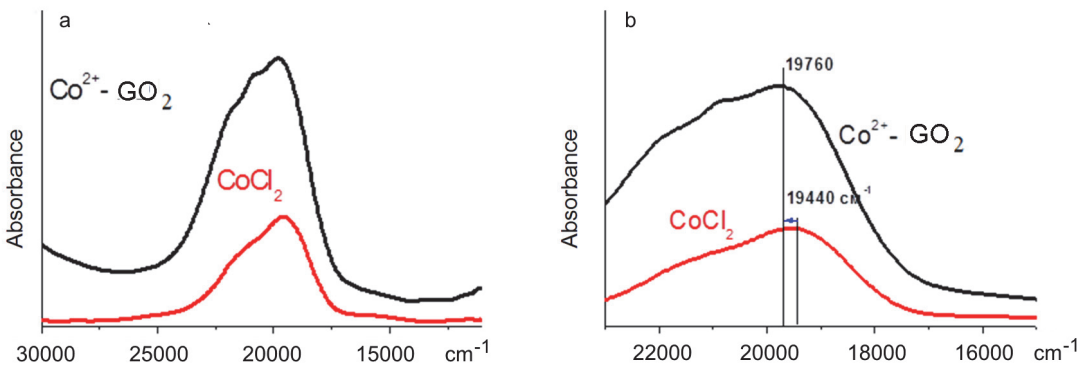


Fig. 5. Electronic absorption spectra of $CoCl_2$ and Co^{2+}–GO.

absorption spectra of the copper complex, there is a broad maximum that corresponds to transitions $B_{1g} \rightarrow E_g$ and $B_{1g} \rightarrow A_{1g}$. The maxima of the absorption bands and the shape of the spectra are characteristic of pseudo-octahedral copper (II) complexes. The shift of the maximum in the complex in the long-wave region compared to copper sulfate indicates a decrease in the degree of axial distortion, which, in this case, is caused by the strengthening of the metal-ligand bond (Table 2, Fig. 3a).

For comparison, Figure 3b shows the UV spectrum of the initial ligand.

Unlike the electronic spectra of the complex and the initial copper salt (Fig. 6), for which the absorption maximum is in the visible region of the ultraviolet spectrum, for the initial ligand, the absorption maximum in the electronic spectrum is in the near ultraviolet region of the spectrum — at 273 nm or 36600 cm^{-1} (Fig. 3b).

Table 2. Electronic transitions of Cu(II) complexes

Compound	$B_{1g} \rightarrow E_g$	$B_{1g} \rightarrow A_{1g}$
$CuSO_4$	–	12320
Cu–GO	14500	13320

A characteristic feature of coordination compounds of nickel (II) (Fig. 4) is the realization of equilibrium between different coordination forms, the most common of which are octahedral complexes of nickel (II). The main transition of nickel (II) ions in octahedral coordination is $^3A_{2g}$. It is known from the diagram of energy levels that three transitions should be observed in the electronic spectra: $^3A_{2g} \rightarrow {}^3T_{1g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(^3F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(^3P)$, but in the frequency range under study we can observe only the last two. The first band is in the long-wave region at a frequency below 10000 cm^{-1}. At 13000 cm^{-1}, the shoulder of the low-intensity forbidden transition $^3A_{2g} \rightarrow {}^1E_g$ is observed. The shape of the electronic spectra indicates a tetragonally distorted octahedral configuration of the nickel ion in the synthesized complexes. The absorption bands of all transitions are slightly shifted to the long-wave region compared to nickel sulfate. This can be caused by both the enhancement of the acceptor properties of the oligomeric ligand compared to

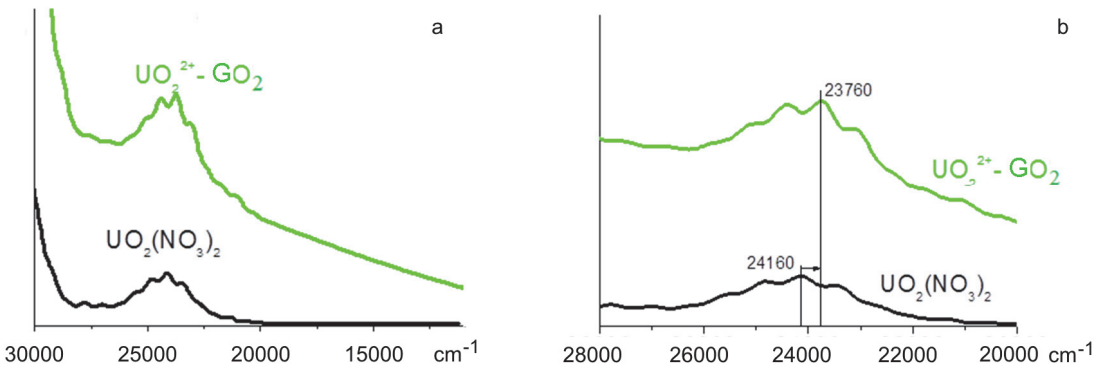


Fig. 6. Electronic absorption spectra of uranyl nitrate and the UO_2^{2+}–GO complex.

nickel sulfate and a decrease in the degree of axial distortion (Table 3, Fig. 4).

In the electronic spectra of cobalt compounds, three *d–d* transitions allowed for spin should be observed: $^4T_{1g}(^4F) \rightarrow {}^4T_{2g}$ (^4F), $^4T_{1g}(^4F) \rightarrow {}^4A_{2g}$ (^4F), $^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$. The first of them has a frequency of 10000 cm^{-1}, that is, it is located in the near-infrared region. The other two transitions are close in energy and can be observed in the visible region of the spectrum. Usually the transitions $^4T_{1g}(^4F) \rightarrow {}^4T_{2g}(^4F)$), $^4T_{1g}(^4F) \rightarrow {}^4A_{2g}(^4F)$, $^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$ appear as a single undivided band, or only the last one is observed. However, in our case, the splitting of the absorption maximum is noticeable in the electronic spectra, which may indicate the presence of both transitions (Fig. 5).

The maximum of the absorption band, which corresponds to the $^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$ transition, is observed in the region of 19000–20000 cm^{-1}. Compared to the spectrum of $CoCl_2$, the spectra of Co–GO_2 show a shift of the maxima to the short-wavelength region at 320 cm^{-1}. Based on the intensity of the absorption bands and maxima in the spectra, it can be concluded that the synthesized complexes have the shape of a distorted octahedron.

Based on the analysis of the bands present in the spectrum of the UO_2^{2+} complex (Fig. 6), it can be argued that the coordination number of uranium is VI. In comparison with the spectrum of $UO_2(NO_3)_2$ salt,

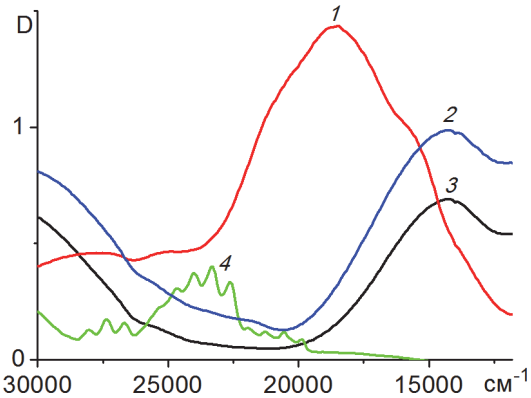


Fig. 7. Diffuse reflection spectra of obtained complexes: Co–GO (*1*), Cu–GO (*2*, *3*) and UO_2–GO (*4*).

the shift of the absorption bands to the long-wavelength region is observed.

Taking into account that the composition of the complexes in the solution can change due to interaction with the solvent or dissociation of the complexes, we have recorded the electronic diffuse reflectance spectra of the synthesized complexes (Fig. 7). It is worth noting that in most cases, the shape of the spectra of the solutions and polycrystalline samples did not differ, although a slight shift of the absorption band was observed by an average of 250–400 cm^{-1}, which indicates the invariance of the chemical composition of the complexes in solutions and the condensed state (Fig. 7).

Based on the data obtained and the analysis of literature [5–8, 22, 23], it can

Table 3. Electronic transitions of nickel complexes (II)

Compound	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow E_g$
$NiSO_4$	25360	15200	13840
Ni^{2+}–GO_2	25520	15240	13960

be concluded that the complexation of GO with transition metals occurs by guanidine fragments and hydroxyl groups.

Thus, a method for the synthesis of complexes of guanidinium-containing oligoether with transition metals has been developed and their complexation ability towards Cu^{2+}, Ni^{2+}, Co^{2+} and UO_2^{2+} ions has been investigated. It is shown that the synthesized oligomer forms stable complexes with polyvalent metal ions, the coordination number of the latter is 6. The obtained complexes have the form of a deformed octahedron.

References

1. N.M.Dyatlova, V.Ya.Temkina, I.D.Kolpakova, Complexes, Khimiia, Moscow (1970) [in Russian].
2. M.T.Bryk, E.A.Tsapyuk, Ultrafiltration, Naukova Dumka, Kiev (1989) [in Russian].
3. Yu.I.Ditnersky, Baromembrane Processes, Khimiia, Moscow (1986) [in Russian].
4. Yu.I.Dytnerskyi, Yu.N.Zhilin, K.F.Volchek, *Water Chemistry and Technology*, **6**, 401 (1984).
5. E.I.Solomon, D.E.Heppner, E.M.Johnston et al., *Chem. Rev.*, **114**, 3659 (2014).
6. P.J.Bailey, *S. Pace Coord. Chem. Rev.*, **214**, 91 (2001).
7. F.T.Edelmann, *Advances in Organometallic Chemistry*, **57**, 183 (2008).
8. R.Kumar, *Polyhedron.*, **56**, 55 (2013). doi.org/10.1016/j.poly.2013.03.043
9. H.Pasdar, N.Foroughifar, B.Hedayati, *Intern. Journal of Chemistry*, **9**, 49 (2017).
10. R.Molinari, S.Gallo, P.Argurio, *Water Research.*, **38**, 593 (2004).
11. R.Molinari, T.Poerio, P.Argurio, *Chemosphere*, **70**, 341 (2008).
12. K.E.Geckeler, K.Volchek, *Environmental Science&Technology*, **30**, 725 (1996).
13. M.C.Sharma, S.K.Sharma, *Advances in Pure and Applied Chemistry*, **1**, 67 (2012).
14. D.M.Saad, E.M.Cukrowska, H.Tutu, *Toxicological &Environmental Chemistry*, **94**, 1916 (2012).
15. N.N.Sauer, D.S.Ehler, B.L.Duran, *J. Environm. Engin.*, **130**, 585 (2004).
16. E.A.Osipova, *Soros Educational Journal*, **8**, 40 (1999).
17. I.Y.Vointseva, P.A.Gembytskiy, Polyguanidines — Disinfectants and Multifunctional Additives in Composite Materials, Paint industry, Moscow (2009).
18. I.I.Vointseva, *Part 1 Water: Chemistry and Ecology*, **7**, 39 (2011).
19. P.A.Hembytskyi, I.I.Vointseva. Polymeric Biocidal Preparation Polyhexamethyleneguanidine, Polygraph, Zaporizhzhia (1998) [in Russian].
20. M.Ya.Vortman, V.N.Lemeshko, V.V.Shevchenko, *Reports of the National Academy of Sciences of Ukraine*, **12**, 75 (2019).
21. M.Ya.Vortman, V.N.Lemeshko, P.V.Vakulyuk et al., *Polymer Journal*, **42**, 199 (2020).
22. F.T.Edelmann, *Advances in Organometallic Chemistry*, **61**, 55 (2013).
23. K.Majid, R.Mushtaq, S.Ahmade, *Review Journal of Chemistry*, **5**, 969 (2008).