

SYNTHESIS, SPECTRAL CHARACTERIZATION AND STABILITY OF THE NEW Nd (III) AND Co (II) HETEROMETALLIC COMPLEXES WITH AMINOPOLYCARBOXYLIC ACIDS**O.K. Trunova*, A.M. Mishchenko, T.O. Makotryk***Vernadsky Institute of general and inorganic chemistry of the Ukrainian National Academy of Sciences, 32/34, Akad. Palladin av., 03142, Kyiv, Ukraine** e-mail: trelkon@gmail.com

New heterometallic complexes of Nd(III) and Co(II) based on ethylenediaminetetraacetic and ethylenediaminedisuccinic acids have been synthesized. The complexes studied by electron absorption spectroscopy, IR-spectroscopy, and thermogravimetric analysis. The influence of a number of factors on the properties and structure of heteronuclear complexes is discussed. The spectral characteristics of homonuclear and heteronuclear complexes are compared. A theoretical analysis of the geometry of Co(II) and Nd(III) complexes with ethylenediaminesuccinic acid was carried out by the semi-empirical PM7 method. It has been shown that the f-d-complexes are of the folded type, in which the ligand-complexone realizes the maximum denticity to Nd(III), and the Co(II) coordination sphere is formed by bridging edta/edds carboxyl groups and intrasphere water molecules. The Co(II) coordination polyhedron corresponds to a distorted octahedron, and the Nd(III) coordination polyhedron corresponds to a one-capped square antiprism (C_{4v}) with the coordination number Nd(III)=8. During study fixed that heterometallic complexes have the same structure in solutions and in the solid state.

Keywords: heterometallic complexes, cobalt, neodymium, aminopolycarboxylic acids, spectral properties.

INTRODUCTION. The development of modern high technologies is based on the use of new functional materials. This requires the development and application of new or significantly modified known methods for their synthesis, which use new precursors with high reactivity, the direction of action, and economic feasibility. In recent years, researchers have paid attention to finding ways to create new complex compounds that contain two metals of different nature (heterometallic complexes) in one internal coordination sphere. Among studies on the targeted synthesis of heteropolynuclear coordination compounds of lanthanides and transition elements, heterometallic aminopolycarboxylate complexes are of great interest due to their structural diversity and the expansion of

potential areas of their application. Aminopolycarboxylate ligands are multidentate ligands and their important characteristics are the bridging nature of carboxylate groups. [1-4].

In most of the works devoted to the study of heterometallic complexes based on aminopolycarboxylates, the structure of the complexes is determined by X-ray diffraction. The number of heteronuclear compounds of s- and d-elements of $M^I[M^{II}(\text{Hedta})(\text{H}_2\text{O})]_2 \cdot n\text{H}_2\text{O}$ ($M^I=\text{Ca, Mg, Sr, Ba}$; $M^{II}=\text{Cr, Co, Cu}$) is known for the most common and widely studied complex of ethylenediaminetetraacetate (H₄edta) [5 6]. Heterometallic lanthanide lanthanide-polyaminocarboxylate of bismuth $\{\{\text{NdBi}(\text{edta})(\text{NO}_3)_2(\text{H}_2\text{O})_{7;22}\}_n\}$ was synthesized, which is a 3D coordination polymer [7]. Recently, heterometallic complexes of

lanthanides with such elements as Ge, Bi with polyaminocarboxylic acids have been studied as precursors for the synthesis of ultrafine powders of metal oxides and metal nanoparticles [8]. In [9, 10], heteronuclear terbium (neodymium) - germanium (or bismuth) compounds with $H_4\text{edta}$ were synthesized and studied. Their spectral and luminescent characteristics have been studied. It has been shown that 4-*f* luminescence of lanthanide ions is observed in all heteronuclear compounds. Based on the $\text{Na}[\text{Ce}(\text{edta})]$ complex, a two-dimensional heterometallic coordination polymer $\text{Ce}_2\text{Co}_3(\text{edta})_3(\text{H}_2\text{O})_{11} \cdot 12\text{H}_2\text{O}$ was synthesized as a metal-ligand, in which ten Ce(III) atoms are coordinated by six carbon-oxygen atoms, three water molecules and four water molecules forming a curved two-cap antiprism. Each of the Co atoms bonds to two hydrated Ce atoms through trident bridged carboxylate groups, and each Ce(III) atom has three adjacent Co atoms. These fragments are connected in a three-dimensional network of water molecules between the layers through numerous hydrogen bonds [11].

A review article [12] on the stereochemistry of complexonates provides a detailed description of the spatial features of edta complexes with lanthanide (III) ions. All ethylenediaminetetraacetate complexes of lanthanides are mononuclear, the ligands in all the described compounds are hexadentate, and the remaining coordination sites are occupied by water molecules (2, 3 or 4). Among the structurally characterized normal mononuclear complexes of lanthanides with edta is the isostructural series of compounds $\text{Ln}(\text{edta})\text{M} \cdot 8\text{H}_2\text{O}$, which includes potassium salts with $\text{Ln}^{3+} = \text{Nd}, \text{La}, \text{Gd}$, sodium with $\text{Ln}^{3+} = \text{Nd}, \text{Tb}, \text{Dy}, \text{Er}$ and ammonium with $\text{Ln}^{3+} = \text{Nd}, \text{Gd}$. A full structural study was performed for $\text{KLa}(\text{edta}) \cdot 8\text{H}_2\text{O}$, $\text{NaTb}(\text{edta}) \cdot 8\text{H}_2\text{O}$ and $\text{NaDy}(\text{edta}) \cdot 8\text{H}_2\text{O}$. For all the above complexes, the lanthanide ion has a coordination number = 9: Ln^{3+} coordinates 6 donor edta atoms and

three water molecules. Coordinated edta^{4-} anions form a curved trigonal prism with triangular faces. Increasing the size of the metal atom and the length of the Ln-N bonds promote the attachment of three water molecules, which are located in the symmetry of the prism.

There are very few works in the literature on the study of heterometallic complexes of d-f metals with ethylenediaminedisuccinic acid ($H_4\text{edds}$). The neodymium-zinc ethylenediaminedisuccinates were described in [13]. It was shown that in heterometallic complexes the Nd^{3+} ion is bound to two α - and one β -carboxyl groups and a nitrogen atom of the NH group of the ligand, and the coordination sphere of the Zn^{2+} ion is formed by oxygen atoms β -carboxyl group edds, which performs a bridging function, and water molecules. New f-d-heterometallic complexes Pr(III), Co(II), Zn(II) with aminopolycarboxylic acids (ethylenediaminetetraacetic, ethylenediaminedisuccinic) were synthesized and spectroscopically characterized in [14]. It has been shown that f-d-complexes belong to complexes of the "folded" type, in which the ligand-complexon realizes the maximum denticity to Pr(III), and the coordination sphere of the 3d-cation is formed by the chain carboxyl groups of the ligands and intrasphere water molecules.

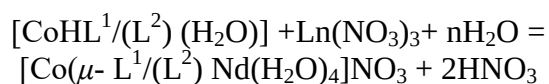
This work presents the results according to synthesis, spectral characterization, and stability of the heterometallic complexes Nd(III) and Co(II) with ethylenediaminetetraacetic and ethylenediaminedisuccinic acids in solutions and in the solid-state.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Neodymium nitrates of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and cobalt $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used for the synthesis of heterometallic complexes with aminopolycarboxylic acids. Ethylenediaminedisuccinic acid was obtained by the condensation reaction of maleic acid with ethylenediamine [15].

Ethylenediaminetetraacetic acid was purchased from Ukrsit LLC (Kyiv) and used without further purification.

Solutions of salts and aminopolycarboxylic acids of the required concentration were prepared according to the exact sample. The concentration of metals in the solutions was determined by complexometric titration (0.01 M) with indicators of murexide (for Co^{2+} ions) and arsenazo 1 (for Nd^{3+} ions).

The synthesis of heterometallic complexes was carried out by the interaction of protonated Co(II) monocomplexes with an inorganic salt of Nd(III) («block» method):



The choice of the method for the synthesis of heterometallic complexes is determined by the values of the thermodynamic stability constants of mononuclear complexes ($\lg K_{\text{st.}}$). When the values of $\lg K_{\text{st.}}$ complexes of $\text{M}^{\text{I}}\text{L}$ and $\text{M}^{\text{II}}\text{L}$ differ by several orders of magnitude, the less stable monometallic complex serves as a “building block” for obtaining a heterobinuclear compound by exocoordination of additional metal ions. In other words, mononuclear complexes act as metal chelate ligands capable of coordinating the second metal ion. It is worth noting that heteronuclear complexes based on complexones were obtained without isolating the “building block” from the solution.

The synthesis of heterometallic complexes was carried out according to the following method. To 100 ml of an aqueous solution of cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 g-mol) was added 200 ml of a solution containing 0.2 g-mol H_4edds (H_4edta) and 2 g-mol NaOH . The resulting mixture (pH ~ 3.5) was stirred intensively for 20 minutes, after which 100 ml of neodymium salt solution (0.1 g-mol) was

added to the reaction mixture. The suspension was heated in a water bath at 50 - 60°C for 1.5 - 2 hours and left to cool. Abundant precipitates of the heterometallic $\text{NdCoL}^{1,2} \cdot n\text{H}_2\text{O}$ complexes (yield of heterometallic complexes 81-86%) fall out of the solutions. The precipitate was filtered and washed with a mixture of ethyl alcohol and acetone (1:1) and dried to constant weight at room temperature (20±2°C). The obtained heterometallic complexes are sparingly soluble in water and other polar solvents.

Investigation of the processes of complexation of neodymium and cobalt ions with aminopolycarboxylates in solutions at their equimolar ratio and $C=1 \cdot 10^{-3} \text{ mol/dm}^3$ was carried out by the method of electron absorption spectroscopy. Electronic spectra were recorded on a Specord M40 spectrophotometer in 1 cm thick quartz cuvettes in the range of 50,000 - 10,000 cm^{-1} . In fig. 1 shows the electronic absorption spectra of complexes Nd(III) and Co(II) with edta (a) and edds (b), and in table.1 - position of the main absorption maxima of Nd^{3+} ions.

In the UV-VIS spectra of aqueous solutions of neodymium-containing complexes (both homo- and heterometallic) range there are narrow bands of characteristic $4f$ -transitions from the basic $^4\text{I}_{9/2}$ -state of the Nd(III) ion (Table 1.1), but for heterometallic complexes the structure of spectra increases, increases the intensity of absorption compared to the spectra of homo-complexes and occurs by shifting the maxima of the bands of the corresponding f - f -transitions in the long-wavelength region ($\Delta\nu_{\text{max}} \approx 170\text{-}190 \text{ cm}^{-1}$ for edds and $\approx 78\text{-}90 \text{ cm}^{-1}$ for edta). This fact indicates the formation of heterometallic complexes, which contain both metals in the internal coordination sphere.

In the $4f$ -absorption spectra of lanthanide complexes, the bands corresponding to the hypersensitive transitions are subject to

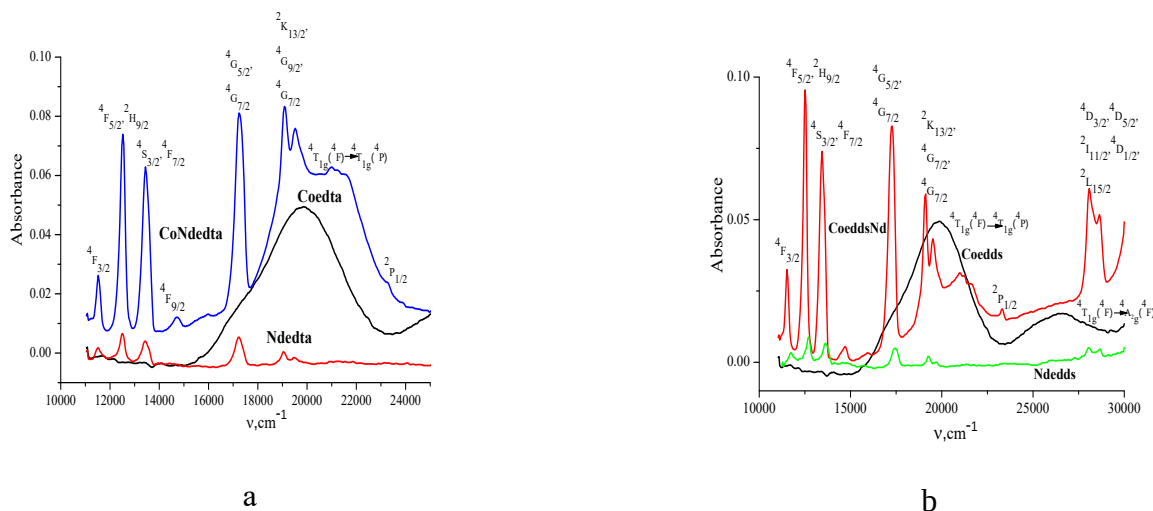


Fig.1. UV-VIS spectra of heterometallic complexes Nd(III) and Co(II) with edta (a) and edds (b) (pH ~ 7; $C=1 \cdot 10^{-3}$ mol/dm³).

Table 1
Transition energies (cm⁻¹) in UV-VIS spectra of Nd(III) and Co(II) complexes with aminopolycarboxylic acids.

Transition	Nd _{aq} ³⁺	Ndedds/Ndedta	NdCoedds/NdCoedta	V _{NdL} -V _{NdCoL}
$4I_{9/2} \rightarrow 2P_{1/2}$	23064	23470/23221	23358/23300,23912	112/79
$4I_{9/2} \rightarrow 4G_{9/2}$	19560	19688/19447	19537/19537	151/90
$4I_{9/2} \rightarrow 4G_{7/2}$	19160	19264/19114	19113/19075	151/39
$4I_{9/2} \rightarrow 4G_{5/2}$	17360	17451/17234	17261/17275	190/45
$4I_{9/2} \rightarrow 4F_{9/2}$	14720	14781/14740	14712/14778	69/38
$4I_{9/2} \rightarrow 4F_{7/2}$	13480	13630/13432	13440/13477	190/45
$4I_{9/2} \rightarrow 4F_{5/2}$	12560	12743/12512	12588/12551	155/39
$4I_{9/2} \rightarrow 4F_{3/2}$	11560	11726/11513	11549/11435	177/78

the greatest influence of the ligand field, so special attention was paid to these bands. Thus, the absorption spectra of neodymium compounds are characterized by two hypersensitive transitions: $4I_{9/2} \rightarrow 2P_{1/2}$ ($v_{\max} \approx 23350$ cm⁻¹) and $4I_{9/2} \rightarrow 4G_{5/2}, 2G_{7/2}$ ($v_{\max} \approx 17400$ cm⁻¹ and 19200 cm⁻¹ respectively). It is worth noting that these bands for ethylenediaminetetraacetate complexes of neodymium are in the lower frequency range than the corresponding bands for ethylenediaminedisuccinate complexes. In this case, the positions of $v_{\max}$ for Ndedta are close

to $v_{\max}$ in the spectra of the aquaion Nd_{aq}³⁺, which may indicate close symmetry of aquacomplexes and complexonates with edta. The Nd complexes with edds have a much larger hypsochromic shift of the absorption maxima of *f-f* transitions compared to Nd_{aq}³⁺, which is caused by a decrease in mutual electron repulsion (nepheloxetic effect) due to the presence of a chiral CH-carbon atom in the edds molecule.

For heterometallic complexes, the $4G_{5/2}$ transition frequency in the spectra of the NdCoedds complex is shifted by 190 cm⁻¹ to the

low-frequency region relative to the corresponding transition to the UV-VIS spectra Ndeds, while for NdCoedta $\nu_{\max}$ this transition is shifted by 45 cm^{-1} in the high frequency region. In this case, for both heteronuclear complexes, the band $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ does not undergo cleavage, which is characteristic of compounds with low symmetry [16]. In the heteronuclear complex NdCoedta, splitting of the $^4I_{9/2} \rightarrow ^2P_{1/2}$ band is observed, which is a consequence of the decrease in the symmetry of the Nd (III) coordination polyhedron in the heteronuclear complex. In the spectrum of the complex NdCoeds for the $^4I_{9/2} \rightarrow ^2P_{1/2}$ transition only one band is observed, which indicates the existence of one type of compound in solution. The shift of the maximum of this band is 112 cm^{-1} , which is typical for complexes with low coordination numbers.

In the UV-VIS spectra of heterometallic complexes, not only the change in the $\nu_{\max}$ position of the Nd(III) ion is observed, but also the $\nu_{\max}$ position of the Co(II) ion changes significantly. If monometallic cobalt complexes are characterized by the presence in the electronic absorption spectra of $d-d$ transitions maxima of Co^{2+} ion at 19844 cm^{-1} (transition $^4T_{1g}(^4F) \rightarrow ^4T_{1g}(^4P)$) and 26480 cm^{-1} (transition $^4T_{1g}(^4F) \rightarrow ^4A_{2g}(^4F)$), then in the electronic spectra of heterometallic complexes the last transition disappears, and for the term $^4T_{1g}(^4F) \rightarrow ^4T_{1g}(^4P)$ a significant hypsochromic shift ($\nu_{\text{CoL}} - \nu_{\text{NdCoL}} \approx -1190\text{ cm}^{-1}$) is observed compared to Coeds (edta). In addition, the specified maximum for heteronuclear compounds is split into 3 components (20999, 21233, 21657 for CoedsNd and 20994, 21341, 21570 cm^{-1} for CoedtaNd), which may indicate a change in the coordination environment of cobalt ions and the existence of heteronuclear compounds of several differently coordinated cations of Co(II). However, the position of the $d-d$ transitions for the Co^{2+} ion in heterometallic

complexes corresponds to the octahedral environment, regardless of the type of aminopolycarboxylic ligand.

In order to obtain information on the quantitative composition of metals included in the internal coordination sphere of complexes formed in the system Co(II) - eds - Nd(III), the dependence of optical density on the concentration of one of the metals at constant concentrations of ligand and second metal and $\text{pH} \sim \text{const}$ (7) (Fig. 2).

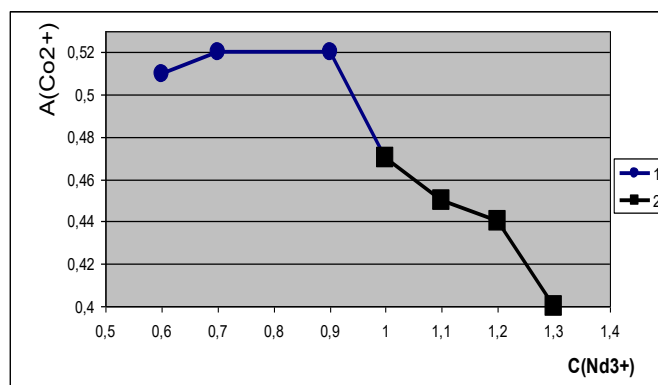


Fig. 2. Composition of heterometallic complex CoedsNd by the method of additives.

As seen from Fig. 2, the value of optical density relative to the concentrations of both Co^{2+} (curve 1) and Nd^{3+} (curve 2) varies in the same way: with increasing concentration of metals from $0.5 \cdot 10^{-4}$ to $0.9 \cdot 10^{-4}\text{ mol/dm}^3$ there is a decrease in the values of optical density, and at $C_{\text{Co(II)}} = C_{\text{Nd(III)}} = 1 \cdot 10^{-3}\text{ mol/dm}^3$ on both curves there is a well-defined inflection, which corresponds to the ratio $\text{Co(II)}:\text{eds}:\text{Nd(III)} = 1:1:1$. This clearly indicates that the internal coordination sphere of heterometallic complexes Co(II) and Nd(III) with eds includes one metal of each type.

Oscillator forces (Table 2) were determined for each of the neodymium-cobalt-containing complexes studied, which were determined by the method [17]. As seen from table 1.2, the strength of the oscillators of

Table 2

Experimental and calculated forces of oscillators (P) of transitions $^4I_{9/2} \rightarrow ^{2S+1}L_J$ of Nd(III) ion in UV-VIS spectra and standard error of calculation ($\times 10^6$).

Multiples	Nd(NO ₃) ₃		Nd(edta)		Nd(edds)		Co(edds)Nd		Co(edta)Nd	
	$P_{exp.}$	$P_{calcul.}$	$P_{exp.}$	$P_{calcul.}$	$P_{exp.}$	$P_{calcul.}$	$P_{exp.}$	$P_{calcul.}$	$P_{exp.}$	$P_{calcul.}$
$^4F_{3/2}$	3,43	2,57	3,19	2,57	3,28	2,29	2,15	2,32	1,24	1,70
$^4F_{5/2} + ^2H_{9/2}$	9,97	9,84	9,53	9,38	9,50	9,44	9,25	8,95	7,59	7,19
$^4F_{7/2} + ^4S_{3/2}$	10,81	11,0 ₉	9,98	10,35	10,68	10,88	9,72	10,09	7,99	8,34
$^4G_{5/2} + ^2G_{7/2}$	10,64	10,7 ₂	15,23	15,36	13,50	13,55	12,27	12,37	10,90	10,94
$^4G_{7/2} + ^4G_{9/2}$	6,72	5,25	7,98	5,48	6,07	5,06	6,67	4,94	4,58	3,85
$^4D_{3/2} + ^4D_{5/2} + ^2I_{11/2} + ^4D_{1/2}$	9,90	11,6 ₇	9,82	11,86	8,49	10,11	9,54	10,49	7,21	7,44
root mean square error	1,43		1,91		1,25		1,18		0,60	

the Co(edds)Nd complex exceeds the strength of the oscillators for Co(edta)Nd in 1.15 to 1.4 times. When comparing homonuclear complexes, an increase in P is also observed during the transition from edds to edta. The values of the shift of the band maxima and the increase in the strength of the transition oscillators in the Nd(III) complexes with edds and edta indicate the different nature of the ligand field influence, which may be caused by differences in the coordination environment of the lanthanide ion in the corresponding compounds.

Based on the obtained data according to the Judd – Ofelt theory [18], the intensity parameters Ω_λ ($\lambda = 2, 4, 6$) of the neodymium ion in the complexes were calculated (Table 3).

The parameter Ω_2 and the oscillator power of the supersensitive transition $^4I_{9/2} \rightarrow ^4G_{5/2} + ^2G_{7/2}$ increase in the series Nd(NO₃)₃ < Nd(L)Co < Nd₂L, which indicates a lower local symmetry of the Nd (III) ion in the monometallic complex, compared with heterometal. The parameter Ω_6 decreases in the series Nd(NO₃)₃ > Nd₂L > Nd(L)Co, which may indicate an increase in the covalence of the neodymium-ligand bond in the transition from

Table 3

Judd-Ofelt parameters Ω_λ ($\times 10^{-20}$ cm²).

Compound	$\lambda = 2$	$\lambda = 4$	$\lambda = 6$
Nd(NO ₃) ₃	1,05	5,29	9,32
Nd(edta)	3,18	5,46	8,68
Nd(edds)	2,86	4,51	9,22
Co(edta)Nd	2,56	3,29	7,07
Co(edds)Nd	2,21	4,77	8,51

monometallic to heterometallic complex.

It is known that the parameter Ω_2 is the most sensitive to the immediate environment of the lanthanide ion. The increase in the value of this parameter contributes to both increasing the degree of covalence of bonds with donor atoms and reducing the symmetry of the ion environment. The change in symmetry may be associated with a change in the geometry of the coordination polyhedron of lanthanides, as well as with a change in the structure of ligands while maintaining the geometry of the coordination polyhedron. Nd(III) ionic solutions are dominated by nine-coordinated aqua complexes, the geometry of which corresponds to a highly symmetric three-cap trigonal prism (point symmetry group D_{3h}) [19]. Therefore,

$\text{Nd}(\text{NO}_3)_3$ is characterized by a low value of Ω_2 ($1,05 \cdot 10^{20} \text{ cm}^2$). In the case of the NdL complex, the Nd(III) environment is a one-cap square antiprism (C_{4v}), which is formed by two nitrogen atoms and four oxygen atoms of the ligand, as well as three water molecules (coordination number = 9) [20]. The value of Ω_2 for CoedtaNd compared to Ndedta decreases from $3,18 \cdot 10^{20} \text{ cm}^2$ to $2,56 \cdot 10^{20} \text{ cm}^2$, which indicates an increase in the symmetry of the Nd(III) environment due to the curvature of its polyhedron due to the formation of Co ions with the Edta molecule and water molecules simultaneously. Close values of Ω_2 obtained for the CoeddsNd complex ($2,21 \cdot 10^{20} \text{ cm}^2$) may indicate a similar geometry of the coordination polyhedron Nd(III) in these compounds. Probably, the heterometallic complex coordination polyhedron is close to a one-cap square antiprism (C_{4v}) and is formed by two nitrogen atoms, three carboxylate oxygen atoms of the edds molecule (or four O in the case of edta) and three (two) water molecules (coordination number Nd(III) = 8). The shift of the maximum of the $^4\text{I}_{9/2} \rightarrow ^2\text{P}_{1/2}$ transition band in the synthesized heterometallic complexes to the long-wavelength region and the increase in the intensity of the supersensitive $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2} + ^2\text{G}_{7/2}$ transition also indicates a decrease of the coordination number in the central ion from 9 to 8. That is, 6 places in the inner sphere of the Nd(III) ion are occupied by hexadent anions of complexones, and two places are occupied by H_2O molecules.

The different nature of the coordination of complexon anions in heteronuclear complexes is also reflected in the comparison of the degree of covalence $b^{1/2}$, which is determined by the nepheloxetic effect (Table 4) [21].

As seen from table 4, the covalence of the bond in heterometallic complexes with both edta and edds is approximately the same, but exceeds $b^{1/2}$ for mononuclear complexes ~ 1.1

Table 4

Parameter of normalized electrostatic repulsion of S_{NES} , nepheloxetic ratio β and covalence parameter $b^{1/2}$ (relative to Nd^{3+} in the gas phase, for which $S_{\text{NES}} = 88713 \text{ cm}^{-1}$).

Complex	$S_{\text{NES}}, \text{ cm}^{-1}$	β	$b^{1/2}$
$\text{Nd}(\text{NO}_3)_3$	86134	0.971	0.121
Ndedta	86485	0.975	0.112
Ndedds	85663	0.966	0.113
Co(edta)Nd	85882	0.968	0.126
Co(edds)Nd	85956	0.969	0.125

times, which confirms the conclusion that the covalent component increases in the formation of a heteronuclear complex.

The calculated values of the nepheloxetic parameter β are close to 1, (Table 4), which may indicate high ionicity of the Nd–O bond in both monometallic and heterometallic complexes. But a slight increase in β values in NdL^{1,2} is associated with increasing ionicity of the bond, and with a decrease in the coordination number of neodymium in comparison with hetero-complexes [22].

The general dependence of shifts of the main maxima of the f - f transitions of the Nd^{+3} ion in the synthesized heterometallic complexes in comparison with the monometallic ones looks as follows (Fig. 3).

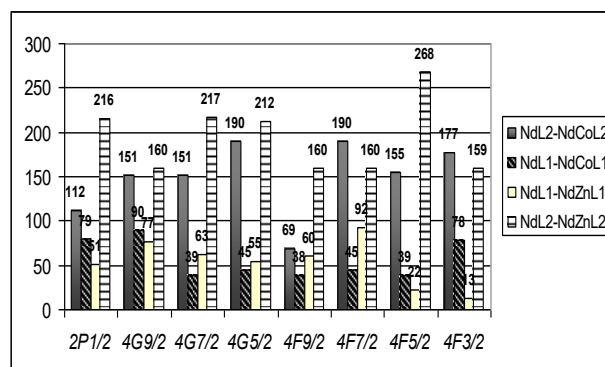


Fig. 3. Diagram of shifts in UV-VIS spectra of heterometallic complexes Nd(III)-Co(II) with aminopolycarboxylic acids (cm^{-1}), $L^1 = \text{edta}$, $L^2 = \text{edds}$.

For the synthesized homo- and heteronuclear lanthanide complexes with L^{-4} anions of complexons, their stability constants were calculated using the mathematical program CLINP [23] (Table 5).

Table 5
Values of stability constants of complexes of Nd(III) and Co(II) with aminopolycarboxylic acids.

Complex	$\lg K_{st.}$
$[NdL^{1-}]$	$16,47 \pm 0,06$
$[NdL^{2-}]$	$14,4 \pm 0,05$
$[CoL^{1-}]^2$	$18,98 \pm 0,06$ [24]
$[CoL^{2-}]^2$	$17,19 \pm 0,05$ [25]
$[NdCoL^{1-}]^+$	$20,1 \pm 0,03$
$[NdCoL^{2-}]^+$	$19,01 \pm 0,04$

Heterometallic complexes are several orders of magnitude more stable than the corresponding monometallic complexes due to the formation of additional bonds, and, accordingly, metal cycles, with donor ligand atoms. The higher stability of heterometallic complexes compared to binary compounds containing the same proton forms of the ligand is associated with the formation of bonds of 2 cations with donor atoms edta/edds, that is, the increase in the stability of the complexonate occurs due to its «crosslinking». Comparison of $\lg K_{st.}$ complexes $NdL^{1,2}$, $CoL^{1,2}$ and $NdCoL^{1,2}$ shows that the difference in the stability of heterometallic and monometallic neodymium-containing complexes ($\Delta \lg K_{NdCoL1-NdL1}=3,63$; $\Delta \lg K_{NdCoL2-NdL2}=4,61$) is several orders of magnitude lower than the corresponding difference between heterometallic and cobalt complexes ($\Delta \lg K_{NdCoL1-CoL1}=1,12$; $\Delta \lg K_{NdCoL2-CoL2}=1,82$). This is probably due to the fact, that in the heterometallic complex the cobalt ion forms much fewer bonds (or cycles) with the donor atoms of complexones than the neodymium ion. That is, $NdCoL^{1,2}$ complexes are «folded» type complexes, in which Co(II)

complexes will play the role of exo-coordinated ligands in the formation of heterobinuclear complexes, and the Co^{2+} coordination sphere in the heteronuclear compounds will be formed only by oxygen atoms of capacious carboxyl groups of ligands and water molecules. The stability of complexes with edds is less than that of the corresponding complexes with edta, which is probably due to different sizes and numbers of chelate metallocycles, as well as to deformation of six-membered β -alanine rings in ethylenediamine disuccinate complexes [14].

Solid samples of synthesized heterometallic complexes were studied by IR-spectroscopy. IR-spectra were recorded on a spectrophotometer Specord M-80 in the range of $4000-400\text{ cm}^{-1}$ in tablets with KBr. The hydrate composition of the synthesized complexes was determined by thermogravimetric method. The thermogravigrams were recorded on a derivatograph Q - 1500°D F. Paulik, J. Paulik, L. Erdey in the temperature range $20-500^{\circ}\text{C}$ with a heating rate of $5^{\circ}/\text{min}$ in a platinum crucible in the presence of the carrier Al_2O_3 (anhydrous).

The thermolysis of the studied heterometallic complexes $NdCoL^{1/2}$ occurs in the same way and has a stepwise character. (Table 6).

At the first stage of thermolysis in a wide range of temperatures ($80-160^{\circ}\text{C}$) is their dehydration, which is accompanied by endothermic effects. In the region of $80-100^{\circ}\text{C}$, a decrease in the mass of complexes is observed due to the detachment of two outer-water molecules, which is accompanied by insignificant endothermic effects. With a further increase of the temperature ($120-180^{\circ}\text{C}$), the removal of H_2O molecules, which are part of the internal coordination sphere of the complexes, takes place.

Different dehydration temperatures

Table 6

Thermal stability of heterometallic complexes Nd(III) and Co(II) with aminopolycarboxylic acids.

Complex	The process of dehydration				t destruction, °C	
	t, °C/ thermal effect	Loss of mass, %		nH ₂ O		
		Calcul.	Experiment.		beginning	close
[NdCoL ¹] ⁺	105/ (endo)	4,48	4,59	2	213	485
	114/ (endo)	7,51	7,59	3		
	153/ (endo)	7,51	7,54	2		
[NdCoL ²] ⁺	92/ (endo)	7,00	7,12	2	220	475
	117/(endo)	7,00	7,46	3		
	155/ (endo)			3		

Table 7

Basic oscillation frequencies in the IR spectra of homo- and heteronuclear complexes of Nd(III) and Co(II) with aminopolycarboxylic acids and their assignment (cm⁻¹).

band assignment	Compounds					
	NdL ²	NdCoL ²	CoL ²	NdL ¹	NdCoL ¹	CoL ¹
v(COOH)	1719	-	-	1731	-	1730
v _{as} (COO)	1592	1636 -1620 1548	1650 1583	1650, 1593	1690 1675 1560	
v _s (COO)	1405, 1331, 1310	1410 1329 1312	1492; 1390 1319	1440, 1410 1402, 1385	1470-1358	
v(CH)	2878	2943, 2862 510	2864 2912	2990 2975	2975-2900	
v(M-O)	566, 598, 666	576, 620 687	537;603;626		700 -520	
v (M-N)	458	456	449	458	457	
n(H ₂ O) _{intra}	3262	3242	3224		3220	
n(H ₂ O) _{inter.}	3445	3454	3460		3420	

indicate different structural role of water molecules in coordination compounds, due to the formation of a branched system of intra- and intermolecular hydrogen bonds characteristic of metal complexonates [26].

The five intraspherical H₂O molecules, which play different structural roles, removed at higher temperatures (≈120⁰C and 150-190⁰C). Probably, 3 molecules of water, which are cleaved at lower temperatures, are bound to the cation of 3d metal, and two molecules of H₂O

are bound to the lanthanide ion, complementing its coordination sphere to the coordination number 8. In the area t ≈225–300⁰C destruction occurs organic ligands with removal of carboxyl and amino groups in the form of CO₂ and NO₂, respectively. These processes are accompanied by a number of endo- and exo-effects. Complete decomposition of compounds ends at t ≈ 480⁰C.

To determine the nature of the binding of metal ions to the functional groups of aminopolycarboxylic acids, their IR spectra were record-

ed. In fig. 4 as an example, the IR spectra of the Coedds(1) and NdeddsCo (2) complexes are given, and Table 7 shows the main oscillation frequencies in the IR spectra of homo- and heteronuclear complexes of Nd(III) and Co(II) with aminopolycarboxylates.

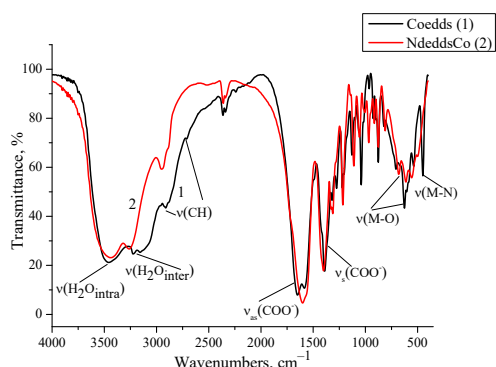


Fig. 4. IR spectra of complexes Coedds(1), NdeddsCo (2).

In the comparative analysis of the IR-spectra of the synthesized heteronuclear complexes and their corresponding metal complexonates, the main attention was paid to the absorption bands corresponding to the oscillations of the functional groups whose donor centers are involved in the binding to cations. In all IR-spectra of complexes with aminopolycarboxylic acids for both monometallic and heterometallic complexes there is a wide band in the range of 3200–3500 cm^{-1} , which corresponds to the valence vibrations of water molecules and indicates the presence of intra- and intermolecular hydrogen bonds. Manifestation of $\nu(\text{OH})$ in the spectra in the form of a doublet indicates that the studied heterometallic complexes contain both external-spherical water molecules and H_2O molecules occupying the intraspherical position. This conclusion correlates well with thermogravimetry data.

In the IR spectra of heterometallic complexes the band of valence vibrations of the free

carboxyl group of aminopolycarboxylates (1731 cm^{-1} for Ndedta and 1719 cm^{-1} for Ndedds) disappears and two split bands of strong intensity $\nu_{\text{as}}(\text{COO}^-)$ appear in the range 1560–1670 cm^{-1} and $\nu_{\text{s}}(\text{COO}^-)$ 1350–1470 cm^{-1} . Compared with the IR-spectra of monometallic complexonates, a shift of these bands to the long-wavelength region is observed. Moreover, the bands ν of oscillations of carboxyl groups in the spectra of heterometallic complexes appear in the form of doublet or triplet bands, which indicates a different coordination environment of complexing metals in hetero- and homometallic compounds. The difference in the position of the oscillation frequencies ν_{s} and ν_{as} of COO^- -groups ($\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$) for heterometallic aminopolycarboxylates is $\sim 200 \text{ cm}^{-1}$ and $\sim 170 \text{ cm}^{-1}$, which indicates the presence of $\text{NdCoL}^{1,2}$ complexes both monodentatically coordinated deprotonated carboxyl groups and the bidentate-bridging nature of their binding [27]. The presence in the low-frequency region of the IR spectra of the multiplet bands in the region 510–700 cm^{-1} , which belong to the $\text{M} - \text{O}$ bond oscillations, also indicates a different coordination of the two cations of the carboxyl groups of the ligands[28].

In the spectra of aminocarboxylate complexes, there are absorption bands in the region of 440–460 cm^{-1} , which correspond to ν oscillations of the $\text{M} - \text{N}$ bond. The $\nu(\text{M}-\text{N})$ oscillation band for the $\text{NdL}^{1,2}\text{Co}$ and $\text{NdL}^{1,2}$ complexes is singlet in nature and has almost the same frequency, which indicates that the Co^{2+} ion is not involved in the formation of this heterobinuclear compound. The presence of metals in the amino groups of ligands is indicated by the presence in the IR spectra of the valence band of the CH groups in the region of 2950–2800 cm^{-1} . This band is one of the criteria for the formation of the coordination link $\text{M}-\text{N}$ in complexes [29]. In the IR spectra of heterometallic complexes, the position of the

$\nu(\text{C—H})$ band does not undergo significant changes with respect to lanthanum-containing homometallic neodymium complexes, which indicates the same coordination of nitrogen atoms in heterocomplexes and $\text{NdL}^{1,2}$. In addition, the multiplicity of $\nu(\text{C—H})$ may indicate the presence in the complexes of an extensive network of intra- and intermolecular hydrogen bonds.

Quantum-chemical calculation of dimeric complexes of Co (II) and Nd (III) from edds of the composition $[\text{Co}_2(\text{edds})_2]^{2-}$ and $[\text{Nd}_2(\text{edds})_2(\text{H}_2\text{O})_4]^{2-}$ was performed by the semi-empirical method PM7 (Sparkle / PM7 for lanthanides) (Fig. 5). For all complexes, the optimized geometries correspond to the minimum on the surface of the potential energy, as evidenced by the absence of negative eigenvalues in their Hessians.

The dimeric complex $[\text{Co}_2(\text{edds})_2]^{2-}$ has the symmetry of the point group C_2 (Fig. 5, a). The immediate coordination environment of each of the Co(II) ions includes 2 nitrogen atoms of the ethylenediamine bridge edds, 2 oxygen atoms of α -carboxyl groups and an oxygen atom of β -carboxyl group. The coordination number of the central ion is supplemented to 6 (curved octahedron) due to the axial oxygen atom of the β -COO- group of the second ligand molecule. There are 3 five-membered chelate cycles in the equatorial plane of the cobalt octahedron: 1 ethylenediamine (Co–N–C–C–N) and 2 glycine (Co–O–C–C–N). The plane of the six-membered β -alanine cycle ((Co–O–C–C–C–N) is in the axial position. The bond lengths in the octahedron $[\text{CoO}_4\text{N}_2]$ are shown in Table 8. According to the results of the calculation, the internuclear distance Co–Co is 6.035 Å. The calculated structure of the $[\text{Co}_2(\text{edds})_2]^{2-}$ complex almost completely coincides with the structure of the cobalt compound with edds $\text{C}_{10}\text{H}_{20}\text{CoN}_2\text{NaO}_{12}$ described in [30, 31].

Neodymium-containing complexes

$[\text{Nd}_2(\text{edds})_2(\text{H}_2\text{O})_4]^{2-}$ have a similar structure to ethylenediamine disuccinate (Fig. 8, b). Since low coordination numbers for lanthanides are uncharacteristic, the coordination number of Nd(III) ions is supplemented by 8 oxygen atoms of two water molecules. The coordination polyhedron $[\text{NdO}_6\text{N}_2]$ is a curved dodecahedron. The Nd–Nd internuclear distance is 7.522 Å.

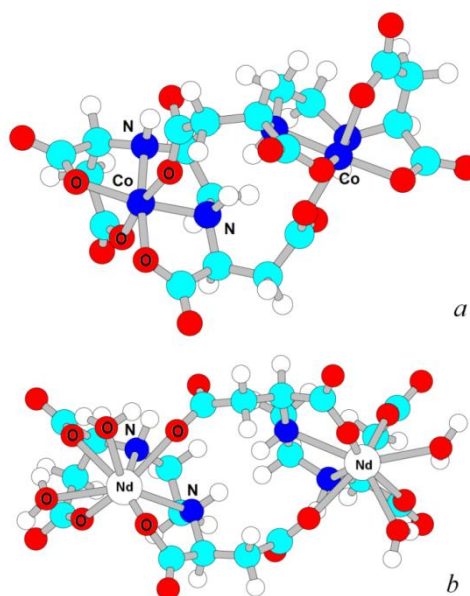


Fig. 5. Optimized structure of complex anions $[\text{Co}_2(\text{edds})_2]^{2-}$ (a) and $[\text{Nd}_2(\text{edds})_2(\text{H}_2\text{O})_4]^{2-}$ (b).

Taking into account the data of IR spectroscopic studies of heterometallic ethylenediamine disinfectants of neodymium and quantum chemical calculations of dimeric complexes $[\text{Nd}_2(\text{edds})_2(\text{H}_2\text{O})_4]^{2-}$, we can assume that in the NdCoL^2 complex in the equatorial positions relative to the Ln^{3+} ion are two nitrogen atoms and two carboxyl oxygen atoms of the edds molecule. Thus two glycine and one ethylenediamine cycles are formed. The six-membered β -alanine ring is located in the axial plane of the neodymium polyhedron. The Co^{2+} ion is bound to the complex ion $[\text{Lnedds}]^-$

Table 8

Calculated bond lengths in polyhedra [CoO₄N₂] and [NdO₆N₂] (Å)

Bond length	Co(II)	Nd(III)
M–N	1,999	2,610
	1,990	2,609
M–O _{α-COO}	1,965	2,377
	1,952	2,350
M–O _{β-COO}	1,951	2,387
M–O _{β-COO} *	1,971	2,420
Nd–OH ₂	–	2,436
		2,341

* β-carboxyl group of an adjacent edds molecule.

through oxygen atoms of the β-carboxyl group, which performs a bridging function. The octahedral configuration of the 3-d metal is supplemented by 3 water molecules.

In heterometallic ethylenediaminetetraacetates NdCoL¹, the edta-ligand is coordinated to the Nd³⁺ ion hexadentate with the involvement of two nitrogen atoms and four carboxylate oxygen atoms. The nitrogen atoms of the ethylenediamine ring and the oxygen atoms of the two 5-membered glycine rings occupy the equatorial plane. The coordination environment of neodymium ions is supplemented by two water molecules. The octahedral coordination polyhedron of cobalt in heteronuclear ethylenediaminetetraacetate is formed by bridged carbon oxygen atoms of bidentate coordinated carboxyl groups of edta anions and three water molecules.

CONCLUSIONS. The f-d-heteronuclear complexes of Nd(III) and Co(II) with aminopolycarboxylic acids were obtained by the method of «block synthesis». The complexes were investigated in solutions and solid - state by methods of electron absorption spectroscopy and IR-spectroscopy. It was found that the pH range 5.5 - 7 is the most susceptible to the formation of heterometallic complexes with deprotonated L^{1,2} anions. In this region, the

absorption spectra of heterometallic complexes in comparison with the spectra of monometallic compounds are characterized by shifting and splitting of the bands of the corresponding *f-f* transitions of Nd³⁺ ion and *d-d* transitions of Co²⁺ ion into the long-wavelength region with a significant increase in absorption intensity. The absorption bands of the Co²⁺ ion partially overlap with the absorption bands of the Co²⁺ ion, which is proof of the formation of heterometallic complexes.

For the NdL^{1,2}, CoL^{1,2} and NdCoL^{1,2} complexes, stability constants were calculated and it was shown that heteronuclear complexes are several orders of magnitude more stable than mononuclear ones due to the formation of additional bonds or metal cycles with donor ligand atoms. The stability of ethylenediaminedisuccinates is lower than that of the corresponding ethylenediaminetetraacetates due to the different sizes and number of chelated metal cycles.

The spectrophotometric characteristics (oscillator power, nepheloxetic effect, Judd – Ofelt parameters) of heteronuclear complexes are compared. It was found that the oscillator forces in edds-based complexes are greater than in edta-based complexes, which is explained by differences in the structure of the coordination environment of the lanthanide ion in the corresponding compounds.

It is proved that f-d-complexes belong to complexes of «folded» type, in which the ligand-complexon realizes maximum dentance to Nd(III), and the coordination sphere of 3-d cation is formed by carboxyl groups edta/edds and intraspherical water molecules. In this case, the Co²⁺ cation is in a curved octahedral environment, and the coordination polyhedron of the neodymium ion corresponds to a one-cap square antiprism (C_{4v}) with a coordination number Ln(III) 8. In solutions and solid - complexants have the same structure.

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СИНТЕЗ, СПЕКТРАЛЬНІ ХАРАКТЕРИСТИКИ ТА СТАБІЛЬНІСТЬ НОВИХ ГЕТЕРОМЕТАЛІЧНИХ КОМПЛЕКСІВ Nd(III) ТА Co(II) З АМІНОПОЛІКАРБОНОВИМИ КИСЛОТАМИ

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Синтезовано та охарактеризовано методами ЕСП, ІЧ-спектроскопії, ДТА нові гетерометалічні комплекси Nd(III) та Co(II) з амінополікарбонowymi кислотами (етилендіамінтетраоцтова, етилендіаміндіантарна кислоти). Показано, що синтез гетерометалічних комплексів доцільно проводити на основі моноядерних полікарбоксилатів 3d-металів, які виступають «будівельним блоком» для отримання гетеробіядерної сполуки з екзокоординацією іонів лантанідів. Комплекси досліджено у розчинах та твердому стані. Встановлено, що незалежно від амінополікарбонОВОЇ кислоти, для обох гетерометалічних систем спостерігається батохромний зсув максимумів поглинання відносно максимумів поглинання гомоядерних комплексів. Для комплексів NdL^{1,2}, CoL^{1,2} та NdCoL^{1,2} розраховано константи стійкості та

показано, що гетероядерні комплекси на кілька порядків стійкіші моноядерних за рахунок утворення додаткових зв'язків або металоциклів із донорними атомами лігандів. Стійкість етилендіаміндисукуцинатів менша, ніж у відповідних етилендіамінтетраацетатів, що пов'язано з різними розмірами і кількістю хелатних металоциклів. Для надчутливих переходів Nd(III) (⁴I_{9/2}→²P_{1/2} та ⁴I_{9/2}→⁴G_{5/2}+²G_{7/2}) розраховано спектральні параметри: сила осциляторів, нефелоксетичний параметр, параметри Джадда – Офельта і ковалентності та показано, що при переході від моно- до гетерометалічного комплексу в ряду аква-іон Ln(III) > гомометалічний комплекс > гетерометалічний комплекс зростає ковалентність зв'язку лантанід – ліганд, а зниженням локальної симетрії іона лантаніду відбувається в ряду аква-іон Ln (III) < гетерометалічний комплекс < гомометалічний комплекс.

Гетероядерні комплекси на кілька порядків стабільніші за одноядерні за рахунок утворення додаткових зв'язків або металоциклів з атомами донорного ліганду. Відзначено, що стійкість комплексів з edds нижча, ніж у відповідних комплексів з edta через різний розмір і кількість хелатних металоциклів. Проведено теоретичний аналіз геометрії комплексів Co(II) та Nd(III) з етилендіаміндіантарною кислотою напівемпіричним методом РМ7.

Показано, що f-d-комплекси належать до комплексів згорнутого типу, в яких ліганд-комплексон реалізує максимальну денатність до Nd(III), а координаційна сфера Co(II) формується містковими карбоксильними групами edta/eds та внутрішньосферними молекулами води. Координаційний поліедр Co(II) відповідає викривленому октаедру, а координаційний поліедр Nd (III) відповідає одношарковій квадратній антипризмі (C_{4v}) з КЧ Nd(III) =8. У розчинах та

твердому стані гетерометалічні комплекси мають однотипну будову.

Ключові слова: гетерометалічні комплекси, кобальт, неодим, амінополікарбонові кислоти, спектральні властивості.

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