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Complexes of Cu(II), Co(II), and Zn(II) Terephthalates with Hydroxyalkylamines

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Abstract—The reactions of Cu(II), Co(II), and Zn(II) terephthalates with hydroxyalkylamines (tris(2-hydroxyethyl)amine, bis(2-hydroxyethyl)amine, tris(hydroxymethyl)aminomethane, and bis(2-hydroxyethyl)aminotris(hydroxymethyl)methane) are studied for the first time. The structures and properties of the synthesized complexes are studied by IR spectroscopy, electronic absorption spectroscopy, mass spectrometry, and elemental and thermal analyses. The structure of the binuclear heteroligand $[Cu_2(TEA)_2(Tph)]_n \cdot H_2O$ complex is studied by single-crystal X-ray diffraction (XRD) (CIF file CCDC no. 2224437).

Keywords: metal-organic frameworks, coordination polymers, hydrometallatranes, hydroxyalkylamines, terephthalic acid, crystal structure

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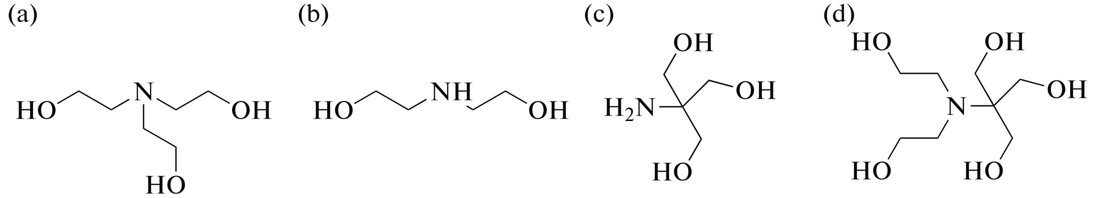
INTRODUCTION

Investigation of atranes, intracomplex compounds of hydroxyalkylamines widely studied by the scientific school guided by Academician M.G. Voronkov, remains to be of considerable fundamental and practical interest [1–3]. In the series of atranes, the complexes of tris(2-hydroxyethyl)amine (TEA) and its structural analogs with transition metal salts is accepted to be distinguished as a particular class named hydrometallatranes by M.G. Voronkov [2, 3]. The studies of biological activity of hydrometallatranes made it possible to find in this series lowly toxic highly efficient substances (LD_{50} 675–4000 mg/kg) having both immunostimulating and immunodepressive properties [4, 5]. R. Kumar and coauthors showed that the silver(I) picrate complexes with hydroxyalkylamines exerted a high antimicrobial effect against pathogenic gram-positive (*S. aureus*) and gram-negative (*S. marcescens*, *S. japonicum*, and *S. maltophilia*) bacteria [6].

The structures of hydrometallatranes were widely studied by XRD. According to the literature data, the reaction of hydroxyalkylamine (HAA) with a transition metal salt (MX_n) can afford cationic mononuclear complexes $[M(HAA)_2]X_n$ [7–9] and mononuclear heteroligand [10–12] or bi- and polynuclear heteroligand complexes [13–16]. In the most part of cases, TEA acts as a tri- (N,O,O') or tetradentate (N,O,O',O'') ligand. In the polynuclear complexes, hydroxyalkylamine or acid anions are bridging ligands. In the bi- and polynuclear complexes, TEA acts as a linker and loses its hydroxyl hydrogen atoms. The binuclear complexes $[Cu_2(TEA)_2X_2]$ ($X = C_6H_4(OH)COO^-$, $C_6H_5CHCHCOO^-$, $C_6H_4(OCH_3)COO^-$; $C_6H_4SO_2C(O)N^-$) in which TEA is deprotonated at one branch were synthesized [14–16]. Anions of aromatic di-, tri-, and tetracarboxylic acids are widely used for the synthesis of metal-organic frameworks (MOFs) characterized by unique structural and physicochemical properties [17–19]. The MOFs of Cu(II) based on TEA and tetracarboxylic pyromellitic acid were synthesized [20, 21] and exhibited a catalytic activity in the oxidation of cycloalkanes. Dicarboxylic terephthalic acid (H_2Tph) containing two carboxyl groups in the *para*-position is also widely used in the construction of MOFs [22–24]. Chromium(III) terephthalate was shown [25, 26] to have a unique mesoporous structure with the zeolite-like topology.

In this work, we studied the reactions of hydroxyalkylamines TEA, bis(2-hydroxyethyl)amine (DEA), tris(hydroxymethyl)aminomethane (TRIS), and bis(2-hydroxyethyl)aminotris(hydroxymethyl)methane (BIS-TRIS) (Scheme 1, structures a–d, respectively) with Cu(II), Co(II), and Zn(II) terephthalates for the formation of MOFs (**I**–**XII**).



Scheme 1.

EXPERIMENTAL

The following commercial reagents and solvents were used as received: inorganic salts $CuSO_4·5H_2O$ and $Co(NO_3)_2·6H_2O$, and $ZnCl_2$ (AO Vekton, Russia); hydroxyalkylamines TEA (≥98%), DEA (≥98%), TRIS (≥99%), and BIS-TRIS (≥98%) (all Sigma-Aldrich); and terephthalic acid (98%, Sigma-Aldrich).

Elemental analyses to the contents of C, H, and N were conducted by burning the sample in an oxygen flow using a Euro EA3028-HT analyzer (EuroVector, Italy). The percentage content of water in the samples was measured on a PE-9210 coulometric Fischer titrator (cell with a membrane) (Ekroskhim, Russia). The IR spectra of the compounds were recorded in KBr pellets on an FSM 2201 FT-IR spectrometer (Infraspek, Russia) in a range of 4000–500 cm^{-1}. The mass spectra of the complexes were detected on a micrOTOF instrument (Bruker, USA) equipped with an ionic source of the electrospray type (ESI) in the range from 100 to 1000 m/z. Electronic absorption spectra were recorded in aqueous solutions of the complexes in a range of 315–900 nm using a PE-5400VI spectrophotometer (Ekroskhim, Russia) with a spectral gap width of 4 nm at room temperature (optical path length 10 mm). Thermal analysis was conducted on an STA 429 CD setup for simultaneous thermal analysis (Netzsch, Germany) on heating with a rate of 10 deg/min in a dynamic air atmosphere (air flow rate 50 cm^3/min) in the range from 40 to 600°C. The decomposition products were examined on a NetzschQMS 403 C quadrupole mass spectrometer that makes it possible to analyze thermal decomposition products in the range from 1 to 121 atomic charge units.

XRD was carried out on a Rigaku Oxford Diffraction XtaLabSuper Nova HyPix-3000 single-crystal diffractometer at 100 K. The detection was carried out using microfocus CuK_α radiation ($\lambda = 1.54184$ Å). The structure of complex **I** was solved by direct methods and refined using the SHELX program [27] integrated in the OLEX2 complex [28]. An absorption correction was applied empirically in the CrysAlisPro software [29] using spherical harmonics accomplished in the SCALE3 ABSPACK scaling algorithm. The final models include coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included into refinement with fixed positional and temperature parameters, where $U_{iso}(H)$ was established as $1.2U_{eq}(C)$ and C–H 0.99 Å for the CH_2 groups, and $U_{iso}(H)$ was established as $1.2U_{eq}(C)$ and C–H 0.95 Å for the CH groups of the aromatic rings. The positions of the hydrogen atoms of the OH groups were determined from the difference synthesis and fixed during refinement with $U_{iso}(H) = 1.5U_{eq}(C)$ and O–H 0.85 Å. The main crystallographic data and XRD experimental parameters are given in Table 1. The crystal structure of complex **I** was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2224437; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of $[Cu(Tph)(H_2O)_2]_n$. A solution of NaOH (1.05 g, 0.026 mol) in water (40 mL) was added to a solution of terephthalic acid (2.16 g, 0.013 mol) in water (250 mL) on heating (T = 55–60°C) with vigorous stirring. After the complete dissolution of the acid, a solution of $CuSO_4·5H_2O$ (3.25 g, 0.013 mol) in water (50 mL) was added to the formed salt. A light blue precipitate was formed immediately after mixing of the solutions. The reaction mixture was heated for 1.5–2 h with continuous stirring. After the end of the reaction, the light blue precipitate was filtered off, multiply washed with water, and dried in air. The yield of the product was 2.66 g (89%). The content of H_2O was 10.9 ± 1.5%.

Synthesis of $[Zn(Tph)(H_2O)]_n$ was carried out similarly to the synthesis of copper(II) terephthalate using solutions of H_2Tph (2.17 g, 0.013 mol), NaOH (1.05 g, 0.026 mol), and $ZnCl_2$ (1.78 g, 0.013 mol) in water. The reaction product was isolated as a white precipitate. The yield was 2.94 g (96%). The H_2O content was 9.4 ± 0.7%.

Synthesis of $[Co(Tph)(H_2O)_2]_n$ was carried out similarly to the synthesis of zinc(II) terephthalate using solutions of H_2Tph (2.23 g, 0.013 mol), NaOH (1.07 g, 0.027 mol), and $Co(NO_3)_2·6H_2O$ (3.91 g, 0.013 mol) in water. However, a precipitate was formed only after the partial evaporation of the solvent. The reaction product was isolated as a pink precipitate. The yield was 1.94 g (65%). The H_2O content was 10.0 ± 1.2%.

Complexes **I**–**XII** were synthesized by the reactions of the prepared Cu(II), Co(II), and Zn(II) terephthalates with TEA, DEA, TRIS, and BIS-TRIS in water at the molar ratios of the reagents 1 : 2 (com-

Table 1. Crystallographic data and structure refinement parameters for complex **I**

Parameter	Value
Empirical formula	$C_{10}H_{18}NO_6Cu$
FW	311.79
Temperature, K	100(4)
Wavelength, Å	1.54184
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	7.50500(10)
b, Å	7.9688(2)
c, Å	10.88180(10)
α, deg	83.9970(10)
β, deg	89.4920(10)
γ, deg	70.315(2)
V, Å^3	609.16(2)
Z	2
ρ, g/cm^3	1.700
μ, mm^{-1}	2.751
θ_{min}, θ_{max}, deg	4.087, 68.143
Number of independent reflections	2198
Number of reflections with $I > 2\sigma(I)$	2080
R_{int}	0.0338
GOOF	1.042
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.0301, 0.0772
Number of refined parameters	175
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.55

plexes **I–IIIa**, **IV–VIIa**, **VIII–XIa**, and **XII**) and 1 : 3 (complexes **IIIb**, **VIIb**, and **XIb**). The reaction mixture was heated at 65°C for 3 h with continuous stirring. After the end of the reaction, the formed colored solution was slowly evaporated at room temperature. The reaction products were isolated as powders from oily liquids by the addition of diethyl ether. The crystals of complexes **I** and **II** were prepared by the slow evaporation of the solvent at room temperature. The elemental analysis data and yields of complexes **I–XII** are listed in Table 2.

RESULTS AND DISCUSSION

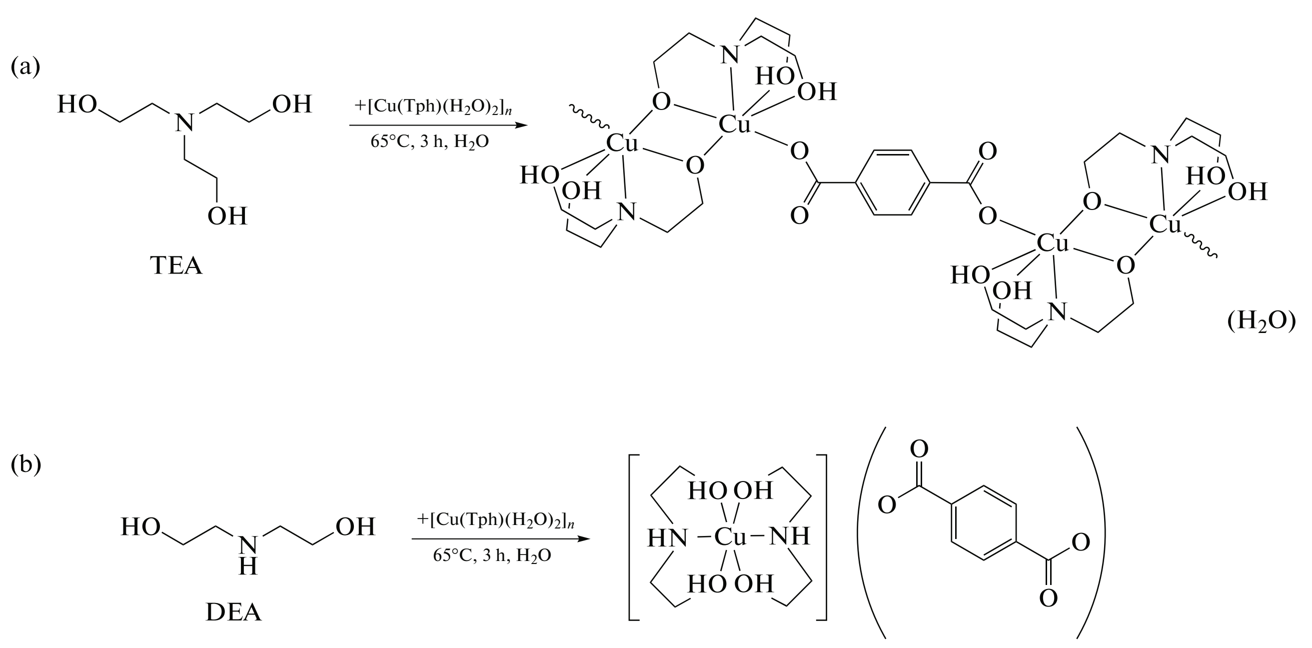
At the first stage, copper(II), cobalt(II), and zinc(II) terephthalates were synthesized by the reactions of sodium terephthalate with the inorganic Cu(II), Co(II), and Zn(II) salts. According to the published data [30–33], the reactions of terephthalic acid with transition metal salts in water afford MOFs in which metal atoms are coordinated by Tph ligands and water molecules. For instance, the structures of the Cu(II), Co(II), and Zn(II) salts correspond to the compositions $[Cu(Tph)(H_2O)_2]_n$ [30], $[Co(Tph)(H_2O)_2]_n$ [31, 32], and $[Zn(Tph)(H_2O)]_n$ [33]. The coulometric titration results showed that the water content in the synthesized samples was closest to the compositions $[Cu(Tph)(H_2O)_2]_n$, $[Co(Tph)(H_2O)_2]_n$, and $[Zn(Tph)(H_2O)]_n$. The IR spectra of the synthesized salts are characterized by broadened bands of the ν(OH) stretching vibrations of the water molecules with maxima in a range of 3419–3172 cm^{-1}. The absence of bands in a range of 1720–1700 cm^{-1} characteristic of the ν(COOH) stretching vibrations con-

Table 2. Composition and elemental analysis data for complexes **I–XII**

Compound	M	HAA	M(Tph) : HAA	Empirical and chemical formulas	Yield, %	$w(H_2O)$,%	$\frac{\text{Found}}{\text{calculated}}$(%)		
							C	H	N
I	Cu	TEA	1 : 2	$C_{20}H_{36}N_2O_{11}Cu_2$ $[Cu_2(TEA)_2(Tph)]_n{\cdot}H_2O$	65	3.2 ± 0.4	$\frac{40.04}{39.54}$	$\frac{5.96}{5.97}$	$\frac{5.05}{4.61}$
II		DEA	1 : 2	$C_{16}H_{26}N_2O_8Cu$ $[Cu(DEA)_2(Tph)]$	59	0.8 ± 0.2	$\frac{44.23}{43.88}$	$\frac{6.33}{5.98}$	$\frac{6.75}{6.40}$
IIIa		TRIS	1 : 2	$C_{16}H_{30}N_2O_{11}Cu$ $[Cu(TRIS)_2(Tph)]{\cdot}H_2O$	63	3.3 ± 0.5	$\frac{39.88}{39.38}$	$\frac{6.20}{5.78}$	$\frac{6.32}{5.74}$
IIIb		TRIS	1 : 3		55	3.8 ± 0.7	$\frac{39.67}{39.38}$	$\frac{6.16}{5.78}$	$\frac{6.20}{5.74}$
IV		BIS-TRIS	1 : 2	$C_{24}H_{44}N_2O_{15}Cu_2$ $[Cu_2(BIS\text{-}TRIS)_2(Tph)]{\cdot}H_2O$	71	2.6 ± 0.4	$\frac{39.84}{39.61}$	$\frac{6.31}{6.09}$	$\frac{4.18}{3.85}$
V	Co	TEA	1 : 2	$C_{20}H_{36}N_2O_{11}Co_2$ $[Co_2(TEA)_2(Tph)]{\cdot}H_2O$	59	2.9 ± 0.5	$\frac{40.58}{40.15}$	$\frac{6.33}{6.06}$	$\frac{4.59}{4.68}$
VI		DEA	1 : 2	$C_{16}H_{28}N_2O_9Co$ $[Co(DEA)_2(Tph)]{\cdot}H_2O$	61	3.8 ± 0.2	$\frac{42.82}{42.58}$	$\frac{6.75}{6.25}$	$\frac{6.55}{6.21}$
VIIa		TRIS	1 : 2	$C_{16}H_{32}N_2O_{12}Co$ $[Co(TRIS)_2(Tph)]{\cdot}2H_2O$	64	3.4 ± 0.4	$\frac{37.92}{38.33}$	$\frac{6.33}{6.03}$	$\frac{5.30}{5.59}$
VIIb		TRIS	1 : 3		57	3.7 ± 0.3	$\frac{38.46}{38.33}$	$\frac{6.47}{6.03}$	$\frac{5.63}{5.59}$
VIII		BIS-TRIS	1 : 2	$C_{24}H_{44}N_2O_{15}Co_2$ $[Co_2(BIS\text{-}TRIS)_2(Tph)]{\cdot}H_2O$	70	2.4 ± 0.6	$\frac{40.43}{40.12}$	$\frac{6.45}{6.17}$	$\frac{4.13}{3.90}$
IX	Zn	TEA	1 : 2	$C_{20}H_{42}N_2O_{14}Zn_2$ $[Zn_2(TEA)_2(Tph)]{\cdot}4H_2O$	53	10.8 ± 0.3	$\frac{36.59}{36.11}$	$\frac{6.29}{6.36}$	$\frac{4.26}{4.21}$
X		DEA	1 : 2	$C_{16}H_{26}N_2O_8Zn$ $[Zn(DEA)_2](Tph)$	63	0.6 ± 0.4	$\frac{43.92}{43.70}$	$\frac{5.97}{5.96}$	$\frac{6.49}{6.37}$
XIa		TRIS	1 : 2	$C_{16}H_{30}N_2O_{12}Zn$ $[Zn(TRIS)_2(Tph)]{\cdot}2H_2O$	59	3.6 ± 0.5	$\frac{37.72}{37.84}$	$\frac{6.37}{5.96}$	$\frac{5.81}{5.52}$
XIb		TRIS	1 : 3		62	3.9 ± 0.4	$\frac{37.63}{37.84}$	$\frac{6.25}{5.96}$	$\frac{5.64}{5.52}$
XII		BIS-TRIS	1 : 2	$C_{24}H_{46}N_2O_{16}Zn_2$ $[Zn_2(BIS\text{-}TRIS)_2(Tph)]{\cdot}2H_2O$	57	5.0 ± 0.7	$\frac{38.64}{38.47}$	$\frac{6.41}{6.19}$	$\frac{4.06}{3.74}$

firms the complete deprotonation of the acid with the formation of the ν(COO) groups. The bands in spectral ranges of 1574–1542 and 1386–1373 cm^{-1} are attributed to the antisymmetric and symmetric stretching vibrations of the carboxylate groups of the terephthalate anion. The stretching vibrations of the aromatic ring (C_{Ar}) appear at wavenumbers of 1672–1422 cm^{-1}.

At the second stage, we studied the reactions of the synthesized $[Cu(Tph)(H_2O)_2]_n$, $[Co(Tph)(H_2O)_2]_n$, and $[Zn(Tph)(H_2O)]_n$ complexes with TEA, DEA, TRIS, and BIS-TRIS in an aqueous medium at the molar ratio of the reagents 1 : 2 or 1 : 3 (in the case of the complexes with TRIS). The elemental analysis data, yields, and assumed compositions of synthesized complexes **I**–**XII** are listed in Table 2. The scheme of the synthesis of complexes **I**–**XII** is shown for the binuclear complex $[Cu_2(TEA)_2(Tph)]_n \cdot H_2O$ (**I**) and mononuclear complex [Cu(DEA)$_2$](Tph) (**II**) (Scheme 2), whose structure was solved earlier [34]. According to the obtained results, the reactions of Cu(II), Co(II), and Zn(II) terephthalates with TEA afford binuclear complexes of the general formula $[M_2(TEA)_2(Tph)] \cdot nH_2O$ differed by the number of molecules of water of crystallization only. It should be expected that the reactions with the BIS-TRIS ligand also lead to the formation of binuclear complexes, which are similar in structure to the complexes of cobalt(II) pyromellitates with BIS-TRIS: $[Co_2(BIS\text{-}TRIS)_2(C_6H_2(COO)_4)] \cdot 5H_2O$ and $[Ni_2(BIS\text{-}TRIS)_2(C_6H_2(COO)_4)] \cdot 3H_2O$ [19]. In these complexes, each metal atom is coordinated by five nitrogen and oxygen atoms of BIS-TRIS and one oxygen atom of the carboxylic acid anion. In the case of ligands DEA and TRIS, the mononuclear complexes corresponding to the formula [M(HAA)$_2$](Tph) are formed. The elemental analysis data showed that the reactions of the salt with the TRIS ligand at molar ratios of 1 : 2 and 1 : 3 afforded complexes of the same composition.



Scheme 2.

The IR spectra of complexes **I**–**XII** are characterized by broadened bands in a range of 3435–3321 cm^{-1}, which are assigned to the ν(NH) and ν(NH_2) stretching vibrations of the groups of the DEA and TRIS ligands and to the ν(OH) vibrations of the groups of hydroxyalkylamines and water molecules. The bands at wavenumbers of 2977–2828 cm^{-1} are related to the ν(CH_2) and ν(CH) stretching vibrations of hydroxyalkylamines and terephthalate ligands. The asymmetric and symmetric ν(COO^-) stretching vibrations of the terephthalate anion groups appear in ranges of 1581–1557 and 1402–1375 cm^{-1}, respectively. The stretching vibrations of the aromatic ring appear in a range of 1641–1422 cm^{-1}. The IR spectroscopy data for complexes **I**–**XII** are given in Table 3.

The transition from copper(II), cobalt(II), and zinc terephthalates to complexes **I**–**XII** results in the situation where new peaks characteristic of hydroxyal-

Table 3. IR spectroscopy data for complexes **I**–**XII**

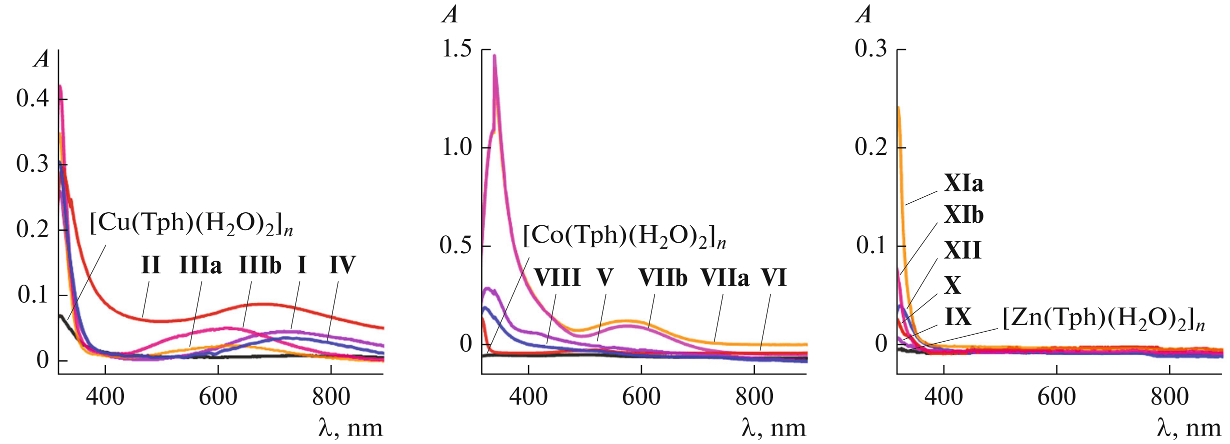
Complex	ν(OH), ν(NH_2) ν(NH)	ν(CH_2), ν(CH)	ν(C_{Ar})	ν_{as}(COO^-)	ν_s(COO^-)
I	3435	2977, 2953, 2902, 2869	1472, 1452	1571	1381
II	3399	2963, 2886, 2832	1487, 1422	1569	1376
IIIa	3321	2947, 2919, 2875	1610, 1462	1560	1380
IIIb	3350	2947, 2919, 2847	1610, 1462	1560	1380
IV	3370	2928, 2883, 2836	1475, 1446	1581	1383
V	3368	2932, 2897, 2832	1485, 1457	1574	1402
VI	3341	2940, 2828	1641, 1472, 1449	1565	1379
VIIa	3340	2944, 2921, 2882	1610, 1456, 1437	1557	1379
VIIb	3370	2937, 2881, 2831	1610, 1462	1561	1382
VIII	3370	2928, 2883, 2836	1475, 1446	1581	1383
IX	3364	2969, 2932, 2897, 2830	1485, 1451	1563	1384
X	3341	2932, 2844	1641, 1468, 1448	1561	1376
XIa	3348	2945, 2919, 2844	1610, 1461	1562	1380
XIb	3349	2943, 2920, 2851	1610, 1482	1560	1381
XII	3350	2964, 2925, 2886	1461, 1442	1562	1375

kylamines appear in all mass spectra (ESI) of the final products **I**–**XII**: $[TEA + H]^+$ (*m*/*z* 150.11), $[DEA + H]^+$ (*m*/*z* 106.09), $[TRIS + H]^+$ (*m*/*z* 122.08), and $[BIS\text{-}TRIS + H]^+$ (*m*/*z* 210.13). In addition, a series of individual peaks corresponding to fragments of the following ions is observed: $[M(HAA)]^+$, $[M(HAA) + H_2O]^+$, $[M(HAA)_2]^+$, $[M(HAA)_2 + H_2O]^+$, $[M(Tph)(HAA) + H]^+$, and others, where M = Cu, Co, and Zn; HAA = TEA, DEA, TRIS, and BIS-TRIS. This confirms that the reactions afford new coordination compounds containing TEA, DEA, TRIS, or BIS-TRIS as ligands.

The electronic absorption spectra of complexes **I**–**XII** are shown in Fig. 1 in comparison with the spectra of the initial terephthalates of the biogenic metals. The spectra of all complexes **I**–**XII** differ substantially from those of the initial complexes indicating a change in the coordination of the metal atom after the reactions with hydroxyalkylamines. In the studied wavelength range, all complexes are characterized by intense absorption bands with a maximum in a range of 320–340 nm related to the intraligand charge transfer in the Tph ligand. The broadened low-intensity bands above 600 nm in the spectra of copper complexes **I**–**IV** are associated with the *d*–*d* transitions of Cu(II), which are characteristic of octahedral geometry. These maxima appear due to the $^2E \rightarrow {}^2B_1$ transition, whereas the complexes with the trigonal bipyramidal coordination show maxima in the range from 800 nm [35]. The spectra of Co(II) complexes **V**–**VIII** also exhibit broadened bands in the visible range (520–580 nm) related to the *d*–*d* transition of the metal ($^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$). The character of the absorption spectra of complexes **V**–**VIII** is typical of the high-spin cobalt(II) compounds in the octahedral coordination [36]. Since the zinc(II) atom has the d^{10} electronic configuration, the spectra of complexes **IX**–**XII** in the visible range exhibit no bands corresponding to *d*–*d* transitions [37, 38].

Assumed compositions of complexes **I**–**XII** were proposed (Table 2) on the basis of the obtained body of experimental data (elemental composition, IR spectra, and electronic absorption spectra) together with the published data on the structures of the hydroxyalkylamine complexes [7–16, 19, 34].

The structure of complex **I** synthesized by the reaction of TEA with $[Cu(Tph)(H_2O)_2]_n$ was studied by XRD. The structure of the complex corresponds to that of the coordination polymer (Fig. 2). Each copper(II) atom is hexacoordinated by the nitrogen atom and three oxygen atoms from one TEA ligand, the oxygen atom of the deprotonated branch of the second TEA ligand, and the oxygen atom of the COO^- group of the Tph ligand. Two deprotonated oxygen atoms



Complex	Absorption maxima, nm	
I	320	720
II	320, 340	684
IIIa	320	607
IIIb	320	607
IV	320	720

Complex	Absorption maxima, nm		
VI	320	340	557
VI	320	–	524
VIIa	320	340	580
VIIb	320	340	580
VIII	320	340	524

Complex	Absorption maxima, nm	
IX	320	340
X	320	–
XIa	320	340
XIb	320	340
XII	320	340

Fig. 1. Electronic absorption spectra of the initial compounds $[M(Tph)(H_2O)_m]_n$ (M = Cu(II), Co(II), Zn(II), m = 1, 2) and complexes **I**–**XII**.

from two TEA ligands act as bridging ligands linking two copper atoms to form the –Cu–O–Cu–O– cycle. The Cu···Cu distance is 2.9043(3) Å. The Tph ligands act as linkers binding the $\{Cu_2(TEA)_2\}$ fragments into infinite chains along the *c* axis (Fig. 3). The water molecules additionally stabilize the crystal structure of the complex forming hydrogen bonds with the hydroxyl groups of TEA from the adjacent polymer chains (Table 4).

It should be mentioned that the complex with a similar structure was synthesized [39] by the reactions of aqueous solutions of $Cu(NO_3)_2 \cdot 2.5H_2O$, TEA, and NaOH with terephthalic acid in an aqueous solution of NaOH. Thus, the formation of the binuclear polymer complex $[Cu_2(TEA)_2(Tph)]_n \cdot H_2O$ is most probable regardless of the synthesis method.

The thermal properties of some synthesized complexes were studied in a temperature range of 40–700°C. The thermal destruction of all studied compounds begins below 210°C. Among them, the complexes with the BIS-TRIS ligand (**IV**, **VIII**, and **XII**) turned out to be most thermally stable. A similar tendency was observed for the complexes of Cu(II), Co(II), and Ni(II) pyromellitates with hydroxyalkylamines [19]. The character of the thermal destruction of the studied compounds is typical of the hydroxyalkylamine complexes [9, 14, 40]. Prior to the thermal destruction, the complexes with TEA, DEA, and BIS-

Table 4. Geometric parameters of hydrogen bonds in complex **I**

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(5)–H···O(3)	0.80	2.04	2.819(2)	166(3)
O(5)–H···O(4)	0.82	2.11	2.886(2)	159(3)
O(6)–H···O(5)	0.83	1.86	2.680(2)	172(3)
O(3)–H···O(7)	0.83	1.78	2.601(2)	170(3)

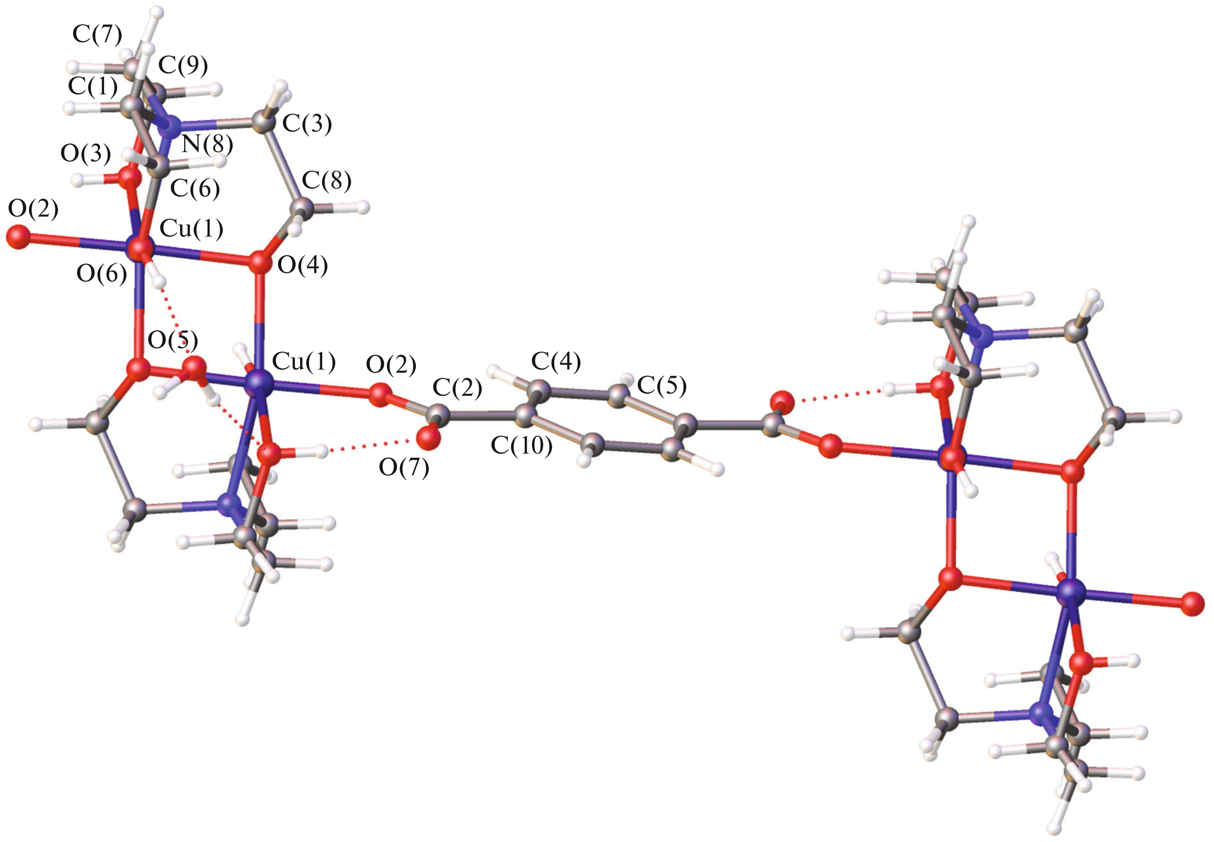


Fig. 2. Molecular structure of binuclear complex **I**.

TRIS experience melting, and a small endothermic effect appears on the DSC curve in a temperature range of 125–165°C. The exceptions are the complexes with TRIS, whose active mass loss starts without melting. Several steps of mass loss can be distinguished on the thermogravimetric curves. They are accompanied by minor exo- or endothermic effects in a range of 190–303°C in the first step and strong exothermic effects in the final step in a temperature range of 336–565°C corresponding to the combustion of organic moieties.

Thus, the reactions of Cu(II), Co(II), and Zn(II) terephthalates with the polydentate N,O-donor ligands TEA, DEA, TRIS, and BIS-TRIS were studied for the first time. The reactions with hydroxyalkylamines can result in the formation of binuclear complexes with the polymer structure or cationic mononuclear complexes depending on the starting hydroxyalkylamine. Regardless of the structure, the thermal destruction of the complexes begins below 210°C. The synthesized polymer complex $[Cu_2(TEA)_2(Tph)]_n \cdot H_2O$ was classified as metal-organic frameworks and formed due to the dissociation of two TEA ligands at one hydroxyethyl branch, which acts as a bridging ligand.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

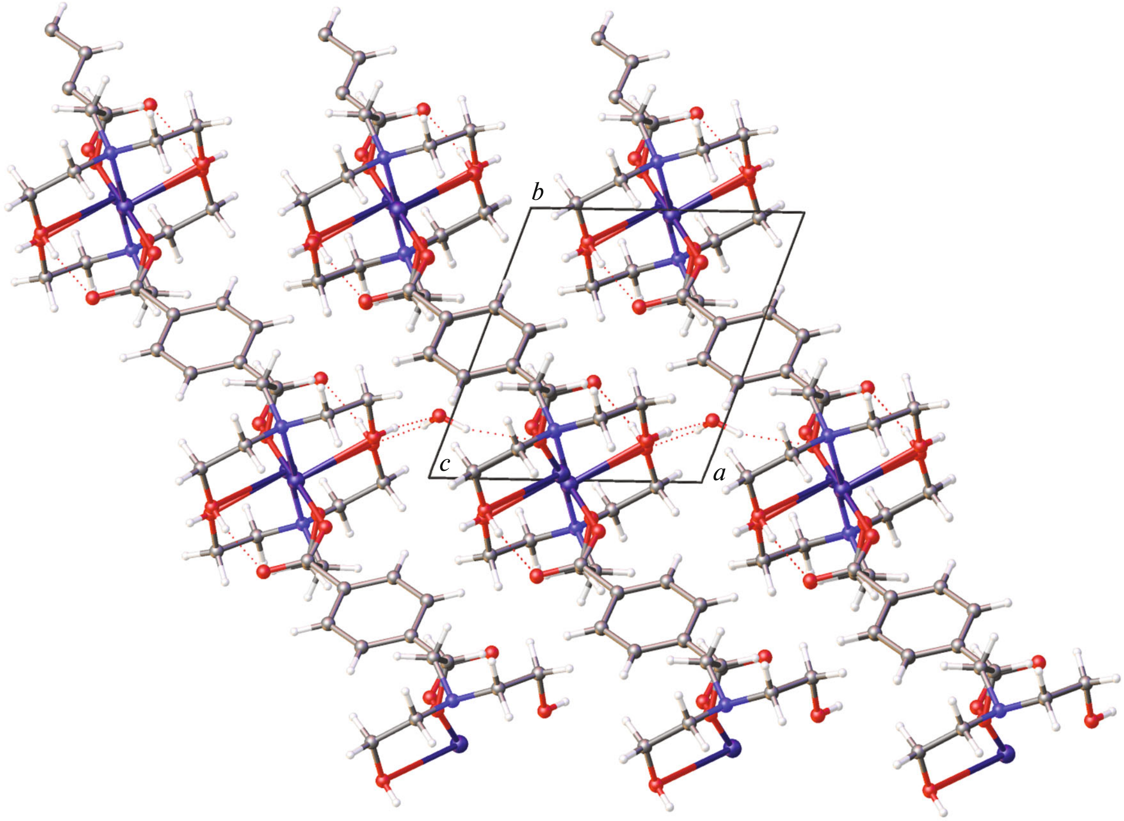

Fig. 3. Packing fragment in the crystal of complex **I**.

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