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CRYSTAL STRUCTURE OF THE MIXED-LIGAND COMPLEX OF Co(II) WITH SUCCINIC ACID AND PYRIDINE

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A new mixed-ligand complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ was synthesized via the interaction of equimolar amounts of cobalt nitrate and sodium succinate in the presence of pyridine at pH 5.5–6.0. The complex was investigated by X-ray structure analysis, elemental analysis, UV/VIS and IR spectroscopies, and differential thermal analysis. The complex is a one-dimensional coordination polymer and crystallizes in the orthorhombic space group Pbca with unit cell parameters a=11.8945 Å, b=8.9064 Å, c=15.1116 Å, $\alpha=\beta=\gamma=90^0$. The atom of cobalt has a slightly distorted octahedral N_2O_4 environment and forms Co–N bonds with two molecules of pyridine and Co–O bonds with the carboxyl groups of two symmetric succinic acid molecules. The coordination number Co(II) is supplemented up to 6 by two water molecules, which are located in the axial plane of the coordination polyhedron. Due to the monodentate coordination of two symmetrically independent carboxylate oxygen atoms of one succinic acid molecule, one-dimensional coordination polymer chains are formed. Polymer chains in the crystal are united by intermolecular hydrogen bonds, which leads to the formation of layers packed in the crystal parallel to the (001) plane. Hirschfeld surface analysis and two-dimensional fingerprint plots were used to analyze the intermolecular interactions present in the crystal.

Keywords: mixed-ligand complexes, cobalt, succinic acid, pyridine, crystal structure.

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Introduction

One of the ways to purposefully model the properties of coordination compounds of transition metals is to obtain mixed-ligand (heteroligand) complexes (MLC). It is known that mixed-ligand complexes of 3d metals are precursors for the creation of functional materials: molecular magnets, fluorescent sensor materials, biologically active compounds, and catalysts [1].

Complexes of cobalt are an important group of coordination compounds, thanks to its biological activity and due to the magnetic and spectroscopic properties of its compounds [2]. Cobalt has a high coordination ability to O-, N-donor ligands, such as Schiff bases, carboxylic acids, β-diketones, derivatives of bidentate or tridentate donor hydrazones, and aromatic amines [3]. However, in most cases, the coordination sphere of Co(II) in these complexes is not completely saturated with ligand donor groups. Therefore, on their basis, it is possible to obtain mixed-ligand complexes, in which the donor atoms of additional ligands will serve as elements to complete the structure in order to maximize the use of the coordination ability of the central atom.

Synthesis of mixed ligand complexes containing various functional groups and donor centers, such as carboxylic acids, amino acids, aromatic nitrogen-containing heterocycles, and pyridine-carboxylic acid

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derivatives, are of special interest. Among the wide variety of carboxylic acids, succinic acid ($H_2C_4H_4O_4$) deserves the most attention, the dianions of which can be mono- or bidentately chelated to metal ions. In addition, due to structural flexibility, the carboxyl groups of succinic acid in many complexes exhibit a bridging function, which leads to the formation of new supramolecular structures, coordination polymers with good thermal stability, and crystals of a wide morphology.

Mixed-ligand succinate complexes of Co(II) and Zn(II) containing isonicotinamide, pyrazine, and imidazole as a second ligand, are known [4,5]. The complexes are 1D or 3D coordination polymers. X-ray structural analysis of Co succinate complexes with pyrazine showed that Co(II) has an octahedral environment consisting of three oxygen atoms from each succinate ligand, one water molecule, and two nitrogen atoms from the bridging pyrazine molecule. Asymmetric fragments are combined into a three-dimensional structure by bis-monodentate bridging succinate anions.

Currently, complexes of the metals with pyridinecarboxylate ligands, which combine the functions of N-containing heterocyclic ligands and O-containing carboxylic acids, are widely studied. On the one hand, carboxylate oxygen atoms are easily coordinated to transition ions of metal, forming stable coordination bonds, and, on the other hand, the nitrogen atom of the heterocycle, due to the overlap of a lone electron pair with a vacant metal orbital, forms σ-bonds, which increases the stability of the complexes and their structural diversity. In such compounds, as a rule, five-membered rings are formed by the formation of a chemical bond formed by the metal with the donor atoms of carboxylate-O and pyridine-N in such compounds [2,6,7]. In ref. [7], two new complexes $[Co(5\text{-}Br\text{-}2,3\text{-}Pydc)(H_2O)_3\cdot H_2O]_n$ (1) and $Co(6\text{-}Me\text{-}2,3\text{-}Pydc)(H_2O)_3]_n$ (2) were synthesized by the solvothermal method. Analysis of the single crystal structure showed that Co–N and Co–O bonds are formed in the complexes, and deprotonated ligands are attached to every second atom of the Co as linkers, forming an infinite one-dimensional chain structure.

Thus, the analysis of scientific literature indicates a shift in the attention of researchers from classical monomers to mixed-ligand complexes. This is due to the intensive search for new functional materials: optical and magnetic, biologically active substances, catalysts of technological and biochemical processes. Therefore, the design of new MLCs, including O, N-donor ligands, a comprehensive study of their crystal structure and physicochemical properties may turn out to be effective tools for influencing the functional properties of various new generation materials.

The aim of this work is to study the crystal structure and properties of a mixed-ligand complex of Co(II) with succinic acid in the presence of pyridine.

Experimental

Materials

Cobalt nitrate $Co(NO_3)_2\cdot 6H_2O$ and pyridine used for the synthesis of the mixed-ligand complex of Co(II) were of the grade chemically pure. Succinic acid was of the analytical grade, solution of ammonium hydroxide (10%) NH_4OH was used. The solutions of the salts of required concentration were prepared according to the exact weight.

Methods

Elemental analysis for carbon, hydrogen and nitrogen was performed by the combustion method with a Perkin-Elmer C, H, N 2400 analyzer. The metal contents were determined by atomic absorption using a Philips Pye Unicam 8000 atomic absorption spectrophotometer.

The hydrate composition of the synthesized complex was determined by the method of differential thermal analysis (DTA). Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Q-1500 D type derivatograph (F. Paulik, J. Paulik, L. Erdey system) in the temperature range from 20 to 1000^0C (heating rate 5^0C/min) in a platinum crucible in the presence of anhydrous carrier Al_2O_3 in a static air atmosphere.

IR spectra were recorded using the spectrometer Specord M-80, in the range from 400 to 4000 cm^{-1} in the KBr tablets. The assignment of vibrational frequencies is based on generally accepted data [8].

Electronic absorption spectra (UV-VIS spectra) were recorded on a UV/VIS Specord 210 Plus spectrophotometer (Analytik Jena AG) in the quartz cuvettes with l=1 cm (measurement range 10000–50000 cm^{-1} relative error in the measurement of optical density ±0.05).

Single crystals for X-ray structural analysis of $C_{14}H_{18}CoN_2O_6$ were collected at 296.15 K by the ϕ- and ω-scan method on a Bruker APEX-II CCD diffractometer with graphite-monochromatized MoKα radiation (λ=0.71073 Å). The data were corrected for Lorentz-polarization and absorption effects by multiscan correction with the SADABS. Using Olex2 [9], the structure was solved with the SHELXT [10] structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package [11]. Full-matrix least-squares refinement against F^2 in anisotropic approximation was used for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined using a «riding» model with $U_{iso}=nU_{eq}$ of the carrier atom (n=1.5 for water molecules and n=1.2 for other hydrogen atoms). Relevant crystal data are listed in Table 1 together with refinement details.

Final atomic coordinates, geometrical parameters and crystallographic data have been deposited into the Cambridge Crystallographic Data Centre, 11 Union Road, Cambridge, CB2 1EZ, UK (https://www.ccdc.cam.ac.uk/structures/).

Hirshfeld Surface Analysis (HSA) [12,13] is an effective method to investigate intermolecular interactions in the crystal structure. This technique is unique in its ability to calculate and visually depict these interactions, with each crystal structure producing unique results. The analysis is carried out by entering the crystallographic information file (CIF) of the molecule under investigation into the Crystal Explorer 17.5 software [12].

Table 1

Crystal data and structure refinement for $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$

Empirical formula	$C_{14}H_{18}CoN_2O_6$
Formula weight	369.23
Temperature / K	296
Crystal system	orthorhombic
Space group	Pbca
a / Å	11.8945(2)
b / Å	8.9064(2)
c / Å	15.1116(3)
α / ^{0}	90
β / ^{0}	90
γ / ^{0}	90
Volume / Å^3	1600.88(6)
Z	4
ρ_{calc} g/cm^3	1.532
μ / mm^{-1}	1.104
F(000)	764.0
Crystal size / mm^3	0.238×0.187×0.075
2Θ range for data collection/°	5.392 to 56.99
Reflections collected	19064
Independent reflections	2021 [R_{int}=0.0352, R_{sigma}=0.0213]
Data / restraints / parameters	2021 / 0 / 107
Goodness-of-fit on F^2	1.239
Final R indexes [I>=2σ (I)]	R_1=0.0717, wR_2=0.1231
Final R indexes [all data]	R_1=0.0821, wR_2=0.1269
CCDC	2342393

One of the primary features of HSA is the generation of 3D molecular surface contours and 2D fingerprint plots. These plots and contours form a van der Waals (vdW) surface around the molecule, representing the space that the molecule occupies within the crystal structure. Importantly, contact distances from points on this surface to atoms within (d_i) and outside (d_e) the surface are determined by the various vdW radii of the atoms. These distances can be normalized later (d_{norm}) [13].

This technique provides a detailed view of intermolecular interactions, varying from short to long, in a crystal structure, which are typically induced by hydrogen bond donors and acceptors. The visualization of these interactions is represented by color-coded finger-print plots and contour surfaces, with distances that are shorter or longer than the sum of the vdW radii being depicted in a range from red (shorter) to white and blue (longer). Molecular Hirshfeld surfaces of a monomer in a polymer chain were performed using standard (high) surface resolution with the three-dimensional d_{norm} surfaces mapped to a fixed color scale from −0.807 (red) to 1.110 (blue) Å. Red spots on the surface indicate contacts involved in hydrogen bonding.

Synthesis

The mixed ligand complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ was synthesized by the interaction of equimolar amounts of cobalt nitrate and sodium succinate in the presence of pyridine at pH 5.5–6.0 using the following method. Up to 10 ml of a warm (50^{0}C) solution of $Co(NO_3)_2\cdot 6H_2O$ (0.2 g-mol) was added to 10 ml of a warm aqueous solution of sodium succinate $Na_2C_4H_4O_4$ (0.2 g-mol) and 10 ml of pyridine. The pH of the solution (pH 5.5–6.0) was controlled by adding 10% NH_4OH solution. The resulting solution was kept in a water bath at a temperature of 60^{0}C for 45 minutes and left for a day. After a day at room temperature (20±3^{0}C), brick-red crystals of the composition $C_{14}H_{18}CoN_2O_6$ (yield of 44%) fell out of the solution, suitable for X-ray structural analysis. The results of the chemical analysis are presented below. Calculated (found) (%): C 45.50 (45.52); H 4.87 (4.85); N 7.58 (7.56); Co 15.98 (15.94) for $C_{14}H_{18}CoN_2O_6$ (369.23 g/mol).

Results and discussion

X-ray structural study

According to the X-ray structural analysis, the mixed-ligand complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ is a one-dimensional coordination polymer (Fig. 1). The complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ crystallizes in the orthorhombic space group Pbca with unit cell parameters a=11.8945 Å, b=8.9064 Å, c=15.1116 Å, $\alpha=\beta=\gamma=90^0$. The asymmetric part of the unit cell contains one Co(II) ion, two pyridine molecules, a succinic acid molecule and two water molecules. The Co1 atom and the succinic acid molecule are located in a specific position relative to the center of symmetry. Each crystallographically independent Co1 atom is in an octahedral environment of N_2O_4 and is coordinated by two symmetrical carboxylate oxygen atoms (O1 and O1^1) from two succinic acid molecules, two oxygen atoms from water molecules (O3 and O3^1) and nitrogen atoms (N1 and N1^1) from two pyridine molecules equivalent in symmetry (symmetry code ^{1}1−x,1−y,1−z). Molecules of pyridine are located in the apical plane of the coordination polyhedron, in the equatorial plane there are two oxygen atoms from two succinate ions monodentately located, and two water molecules are in the axial position (Fig. 1).

As a result of monodentate coordination of two carboxylate oxygen atoms (from one molecule of succinic acid) to two symmetrically independent Co ions, one-dimensional coordination polymer chains are formed (Fig. 2). The bond lengths of Co−O1(O1^1) and Co−O3(O3^1) are 2.068(2) Å and 2.099(2) Å, respectively. They are slightly different from each other, which is due to a slight distortion of the octahedron (Table 2). The lengths of the Co−N1 and Co−N1^1 bonds are equal and amount to 2.186(3) Å, which is slightly longer than the equatorial lengths of the Co−O bonds. It should be noted that the average bond lengths of Co−O (2.211 Å) and Co−N (2.235 Å) are close to the corresponding values determined for similar complexes [2,3,5]. Diagonal bond angles O1−Co1−O1^1=180.0^0 and O3−Co1−O3^1=180.00(5)^0, 1−Co1−N1^1=180.00(15)^0 do not deviate from the ideal values of 180^0. The values of the vertex angles O1−Co1−N1^1=O1^1−Co1−N1=88.54(11)^0, O3−Co1−N1=O3^1=Co1=N1^1=91.48(11)^0 have minimal deviations from 90^0, which indicates a slight distortion of the octahedral polyhedron of the cobalt atom.

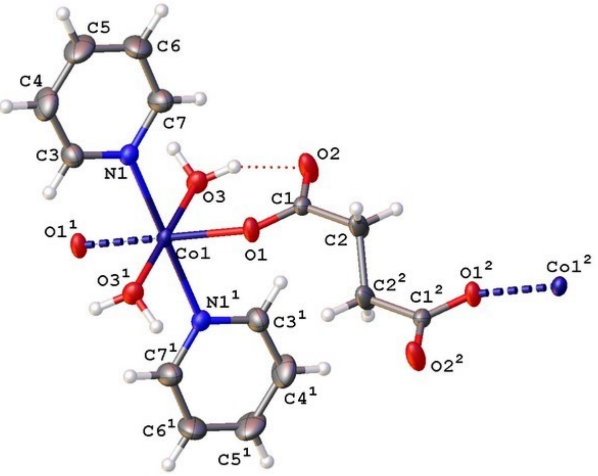


Fig. 1. The molecular structure of the $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ complex. The symmetry operation ^{1}1−x, 1−y, 1−z; ^{2}1−x, 1−y, 1−z

The interatomic distances of Co1−Co1^1 in the chains of the complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ are 8.9064(2) Å and significantly more than the sum of their van der Waals radii (~4.6 Å), which excludes the possibility of weak magnetic exchange interaction between the cations of cobalt.

The crystal contains intramolecular hydrogen bonds between the uncoordinated O2 atom of succinic acid carboxylate and the coordinated water molecule (Fig. 1), the lengths of which are in the range of 1.85−2.689(4) Å.

In the crystal phase, the polymer chains of $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ are located along the crystallographic axis *a*. The intermolecular hydrogen bonds occur between neighboring polymer chains (Table 3), which leads to the formation of layers consisting of polymer chains parallel to the (001) plane (Fig. 3).

Molecular Hirshfeld surfaces of a monomer in a polymer chain were performed using standard (high) surface resolution with the three-dimensional d_{norm}

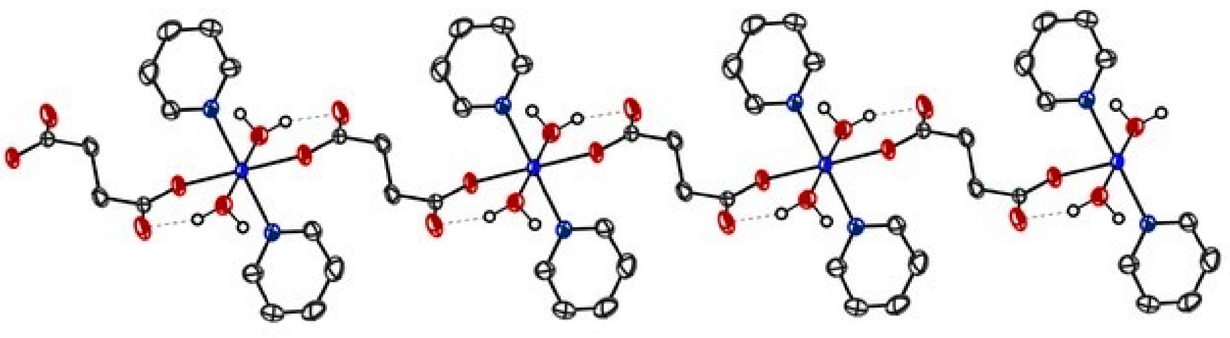


Fig. 2. 1D linear polymer chains built using carboxylate oxygen atoms in the $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ complex

Table 2

Selected bond distances and angles for the $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ complex. (Symmetry code ^{1}1−x, 1−y, 1−z)

Bond	Distance, Å	Bond	Angle, deg
Co1–O3^1	2.099(2)	O1–Co1–O1^1	180.0
Co1–O3	2.099(2)	O3–Co1–O3^1	180.00(5)
Co1–O1	2.068(2)	O1^1–Co1–N1^1	88.54(11)
Co1–O1^1	2.068(2)	O1–Co1–N1	88.54(11)
Co1–N1	2.186(3)	O3–Co1–N1	91.48(11)
Co1–N1^1	2.186(3)	O3^1–Co1–N1^1	91.48(11)
		O1^1–Co1–O3^1	89.12(10)
		O1–Co1–O3	90.88(10)
		O1–Co1–N1	91.46(11)
		N1–Co1–N1^1	180.00(15)

surfaces mapped to a fixed color scale from −0.807 (red) to 1.110 (blue) Å (Fig. 4).

The red spots on the surface correspond to the H···O contacts resulting from the O−H···O hydrogen bonds. It should also be noted that on the Hirshfeld surface of the monomer in the polymer chain, the edge-effect contacts are highlighted in red. This is a metal−O contact that cannot be correctly evaluated but it shown on the Hirshfeld surface. White areas indicate places near the sum of the van der Waals radii of the atoms in consideration and demonstrating the H···H interaction. Blue regions indicate areas where neighboring atoms are too far distanced to interact with each other.

Fingerprint plots of the $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ are shown in Fig. 5. Based on the analysis of the contributions of different types of interactions, it is concluded that H···H interactions make the main contribution to the overall Hirschfeld surfaces and account for 44.3%. The H···O/O···H intermolecular interactions appear as distinct peaks on the two-dimensional fingerprint (d_e+d_i~1.8 Å and two symmetrical points at the top, bottom left and right) and the contribution from total Hirshfeld surfaces is 28.6%. These data are characteristic of O−H···O hydrogen bonds. The C···H/H···C interactions, contributing 20% to the total, are placed above the O−H regions. The other types of interactions such as N···H/H···N (2.8%), N···O/O···N (0.6%), C···C (0.3%) make minor contributions to the total Hirshfeld surfaces.

UV/VIS and infrared spectral study

Electronic absorption spectra of Co(II) complexes with succinic acid and pyridine are shown in Fig. 6.

The position of the main absorption bands in the UV-VIS spectra of the complexes corresponds to *d−d* electronic transitions of the Co(II) ion in a distorted octahedral environment. The absorption maximum (ν_{max}) at ~19600 cm^{-1} corresponds to the $^4T_{1g}(^4F)\rightarrow{}^4T_{1g}(^4P)$ transition. For this term, a bathochromic shift is observed in the spectrum of the mixed-ligand complex compared to the $Co(C_4H_4O_4)$ and $Co(Py)_2$ complexes

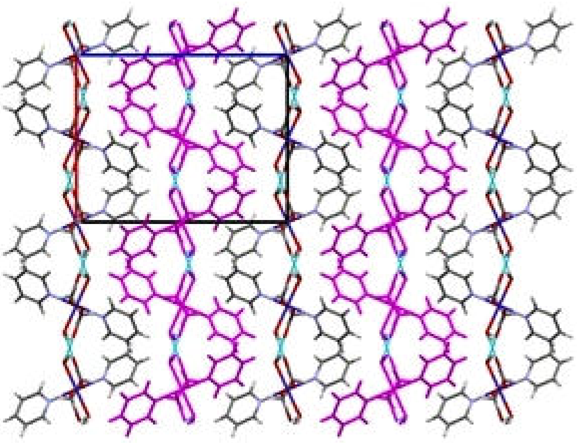


Fig. 3. Crystal packing of $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$. View along the crystallographic *b* axis. Some layers are highlighted in purple

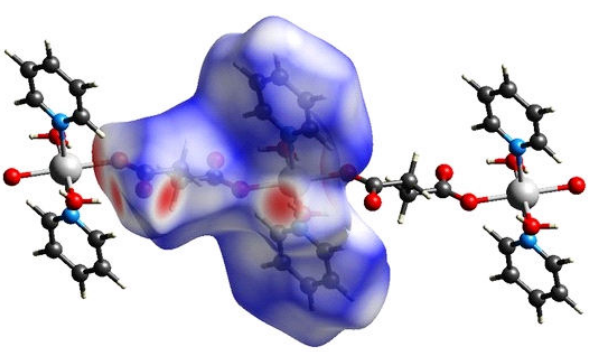
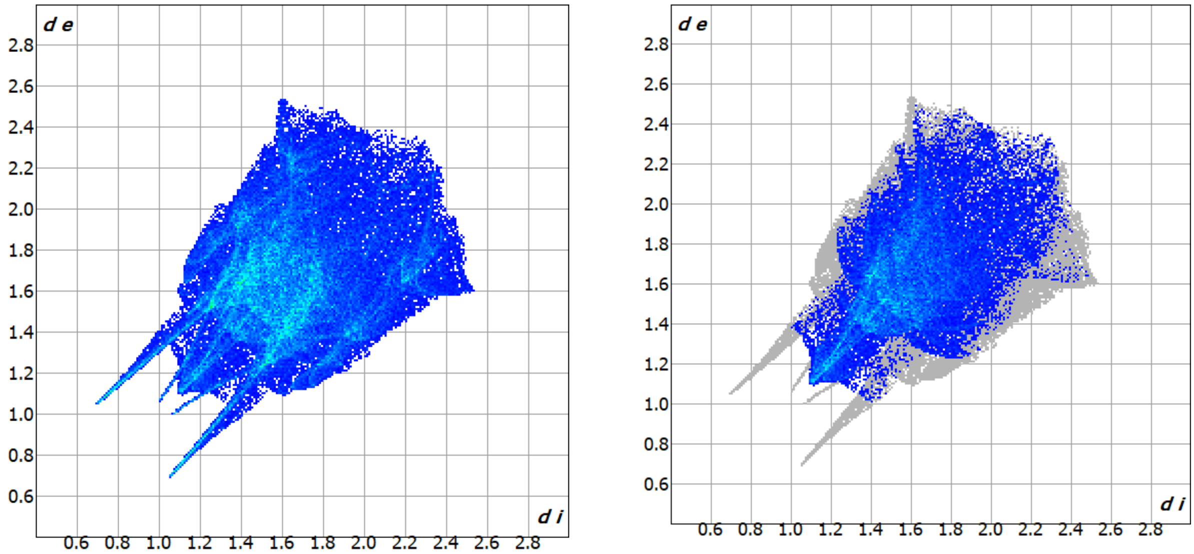
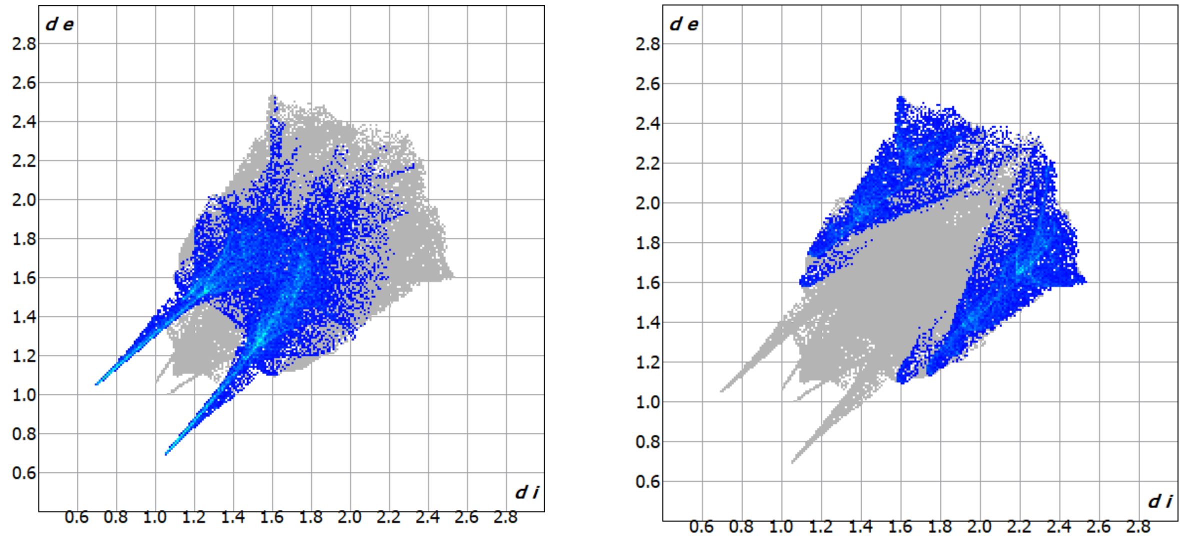


Fig. 4. A fragment of the polymer chain of compound $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ with Hirshfeld surface of monomer mapped with d_{norm}



all

H···H 44.3%



O···H/H···O 28.6%

C···H/H···C 20%

Fig. 5. Two-dimensional fingerprint plots order with a d_{norm} view of the H···H (44.3%), O–H/H···O (28.6%), and C···/H···C (20%) in $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$. Fingerprint plots are given for interactions with a contribution of more than interactions with a contribution of more than 3%

($\nu_{Co(C4H4O4)}-\nu_{\{[Co(C4H4O4)\cdot 2Py]\cdot 2H2O\}n}=61$ cm^{-1}, $\nu_{Co(Py)2}-\nu_{\{[Co(C4H4O4)\cdot 2Py]\cdot 2H2O\}n}=209$ cm^{-1}). This may indicate a weakening of the Co^{2+} bond both with the carboxyl chromophore group of succinate due to coordination of the second ligand, and with the pyridine nitrogen atom due to lengthening of the axial Co–N bond, but the Co(II) coordination polyhedron remains unchanged, as in homoligand complexes. It should be noted that the absorption band in the mixed-ligand complex has a small high-frequency shoulder at 20640 cm^{-1}, which may be a consequence of the distortion of the D_{4h} type octahedral symmetry due to the spin-orbit interaction in the excited state of the $^4T_{1g}$(P) term [14].

Comparison of the IR spectra of the mixed ligand complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ with the spectra of the $Co(C_4H_4O_4)$ and $Co(Py)_2$ complexes (Table 3) shows that the vibration bands of the main functional groups of the ligands in MLC undergo a bathochromic shift. In the regions of 1632–1600 cm^{-1} and 1400–1350 cm^{-1} for succinate complexes, characteristic vibration bands of carboxyl groups are observed, corresponding to asymmetric and symmetric stretching vibrations of coordinated carboxyl groups, respectively. The difference in the position of the ν_sCOO^- and $\nu_{as}COO^-$ bands in the complex

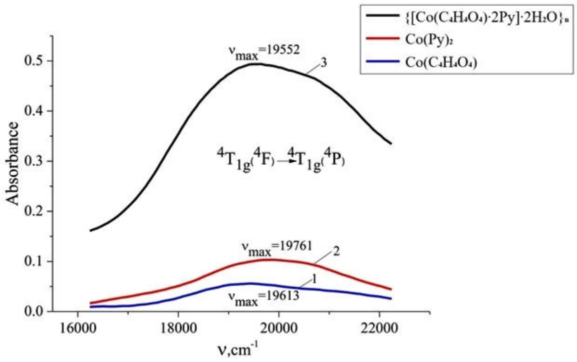


Fig. 6. UV-VIS spectra of complexes $Co(C_4H_4O_4)$ (1), $Co(Py)_2$ (2), $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ (3)

($\Delta\nu$~200 cm^{-1}) indicates the monodentate coordination of the COO^--groups of succinic acid, which is confirmed by the results of X-ray structural analysis of a single crystal $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$.

The small shift of these bands assigned to $Co(C_4H_4O_4)$ indicates that in MLC the coordination of Co(II) with succinate anions is close to the coordination of the central atom in cobalt succinate. However, the increase in the absorption frequency $\nu_s(COO^-)$ in MLC compared to $Co(C_4H_4O_4)$ indicates a purely ionic type of bonding of Co(II) ions with the oxygen atoms of ionized carboxyl groups with an insignificant contribution of the covalent component to the ionic bond. It should be noted that in the IR spectrum of $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$, these bands are detected in the form of multiplets. This is due, on the one hand, to the large number of carboxylate groups in the complex due to its polymer structure. On the other hand, in the region of 1630–1450 cm^{-1}, the in-plane stretching vibrations CN of the pyridine ring overlap with the ν vibrational bands of carboxylates. The presence of intense bands in the IR spectrum of the MLC in the region of 810–650 cm^{-1}, as well as a band at 946 cm^{-1} due to out-of-plane bending vibration (OCO), confirms the coordination of Co(II) by oxygen atoms of succinic acid.

The IR spectrum of the $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ complex in the low-frequency region contains low-intensity singlet absorption bands at 482 cm^{-1} and 467 cm^{-1}, are assigned to stretching vibrations of the M–N bond. This indicates the coordination of the metal with pyridine nitrogen atoms, which is confirmed by the presence of ν(CN) bands in the spectra at higher wave numbers compared to $Co(Py)_2$.

The bands observed in the range from 3126 cm^{-1} to 2875 cm^{-1} are assigned to C–H stretching vibrations of methyl groups.

In the region of 3500–3200 cm^{-1}, the MLC spectrum shows a wide multiplet high-intensity absorption band, which is due to the ν(OH) stretching vibrations of coordinated water molecules. The bands of average intensity in the region of 1150–1008 cm^{-1}, are assigned to δ(OH), confirm the conclusion that the complex contains coordinated water.

Thermal analysis of the complex

The thermal decomposition of the $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ complex was studied by thermogravimetric analysis in air. Thermolysis of MLC is stepwise. At the first stage of decomposition in the temperature range of 120–230^{0}C, dehydration of the complex occurs, accompanied by endothermic effects at 145^{0}C and 198^{0}C. The mass loss (Δm) of the sample corresponds to the detachment of two coordinated water molecules (Δm_{found}=10.0%, and

Table 3

Basic vibrational frequencies (cm^{-1}) and their assignments in the IR spectra of Co(II) complexes with succinic acid and pyridine

Band assignment	$\{[Co(C_4H_4O_4)\cdot 2Py]\cdot H_2O\}_n$	$Co(C_4H_4O_4)$	$Co(Py)_2$
$\nu_{as}(COO^-)$	1634, 1596, 1561, $1545_{sh.}$, 1537, 1521	1640–1530 [4]	–
$\nu_s(COO^-)$	1438, 1400, 1392_{sh}, 1381, 1355	1470-1358 [5]	-
ν(CH)	3126, 2950, 2875	2975-2900 [4-5]	3050–2960
$\nu(CN)_{Py\ ring}$	–	–	1450–1630
ν(NH)	3364	–	3200–3300
δ(OH)	1149, 1103		
$\delta(OH)_{coord.}$	1068, 1038, 1008		
ν(M–O)	809, 796_{sh},702, 658	700–520 [4,5]	–
ν(M–N)	482, 467	–	443
ν(O–H)	3250	3220 [4]	–
$\nu(H_2O)_{inter}$	3487	3420 [4]	–

Δm_{calc}=9.7%). A wide range of dehydration temperatures and a fairly high temperature of the process show that water molecules in the structure of the complex form a branched system of intra- and intermolecular hydrogen bonds. In the temperature range of 230–380^{0}C, the organic part of the molecule is destroyed. At a temperature of 230^{0}C, a small endo-effect is observed on the DTA curve, associated with the removal of two pyridine molecules (Δm_{found}=42.1%, and Δm_{calc}=42.8%). Further thermolysis of the complex at t>250^{0}C is associated with intensive decomposition of cobalt succinate, which is accompanied by a number of endo-effects (278^{0}C, 330^{0}C, and 400^{0}C). It should be noted that succinate decomposes to the oxide without the formation of an intermediate carbonate. This type of thermolysis can be compared to the process of thermal decomposition of succinic acid, which forms succinic anhydride and water when heated. Complete decomposition of the complex ends at t~520^{0}C. In this case, the exo-effects observed on the DTA curves (570^{0}C, 630^{0}C, 690^{0}C, and 735^{0}C) are not accompanied by a change in the mass of the sample and are associated with structural rearrangements in cobalt oxide Co_3O_4, which is the final product of the decomposition of the complex. This conclusion is confirmed by XRF data [15].

Conclusions

A new mixed-ligand complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ was synthesized by mixing of equimolar amounts of cobalt nitrate and sodium succinate in the presence of pyridine at pH 5.5–6.0. The synthesized complex was studied by the methods of electronic absorption spectroscopy, IR spectroscopy, and differential thermal analysis. The structure of the complex was established by X-ray structural analysis of a single crystal. The complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ is a one-dimensional coordination polymer and crystallizes in the orthorhombic space group Pbca with unit cell parameters a=11.8945 Å, b=8.9064 Å, c=15.1116 Å, $\alpha=\beta=\gamma=90^0$. The Co(II) ion is in a distorted octahedral environment and is coordinated by two symmetrical carboxylate oxygen atoms from two succinic acid molecules, two oxygen atoms of water molecules and nitrogen atoms of two pyridine molecules. As a result of monodentate coordination by two carboxylate oxygen atoms of one succinic acid molecule of two symmetrically independent ions of the cobalt, one-dimensional coordination polymer chains are formed. An intramolecular hydrogen bond is observed between the uncoordinated oxygen atom of succinic acid and the coordinated water molecule. In the crystal, the polymer chains $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ are united by intermolecular hydrogen bonds, which leads to the formation of layers packed in the crystal parallel to the (001) plane.

Hirschfeld surface analysis and two-dimensional fingerprint plots were used to analyze the intermolecular interactions present in the crystal. It is shown that the main contribution to the total number of Hirshfeld surfaces is made by H···H interactions, which make up 44.3%. Intermolecular interactions H···O/O···H make up 28.6%, which is characteristic of O–H···O hydrogen bonds. C···H/H···C interactions, which make up 20% of the total, are located above the O–H regions.

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КРИСТАЛІЧНА СТРУКТУРА ЗМІШАНОЛІГАНДНОГО КОМПЛЕКСУ Co(II) З БУРШТИНОВОЮ КИСЛОТОЮ ТА ПІРИДИНОМ

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Синтезовано новий різнолігандний комплекс $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ взаємодією еквімолярних кількостей нітрату кобальту та сукцинату натрію в присутності піридину при pH 5,5–6,0. Комплекс був охарактеризований за допомогою рентгенівського структурного аналізу, елементного аналізу, ЕСП та ІЧ-спектроскопії, диференціального термічного аналізу. Комплекс є одновимірним координаційним полімером і кристалізується в орторомбічній просторовій групі Pbca з параметрами елементарної комірки a=11,8945 Å, b=8,9064 Å, c=15,1116 Å, $\alpha=\beta=\gamma=90^0$. Атом кобальту має злегка спотворене октаедричне оточення N_2O_4 і утворює зв’язки Co–N з двома молекулами піридину і зв’язки Co–O з карбоксильними групами двох симетричних молекул бурштинової кислоти. Координаційне число Co(II) доповнюється до 6 двома молекулами води, які розташовані в осьовій площині координаційного багатогранника. Завдяки монодентатній координації двох симетрично незалежних карбоксилатних атомів кисню однієї молекули янтарної кислоти, утворюються одновимірні координаційні полімерні ланцюги. У кристалі полімерні ланцюги об’єднані міжмолекулярними водневими зв’язками, що приводить до утворення шарів, упакованих у кристалі паралельно площині (001). Для аналізу міжмолекулярних взаємодій, присутніх у кристалі використовували аналіз поверхні Гіршфельда та двовимірні графіки відбитків пальців.

Ключові слова: змішанолігандні комплекси, кобальт, бурштинова кислота, піридин, кристалічна структура.

CRYSTAL STRUCTURE OF THE MIXED-LIGAND COMPLEX OF Co(II) WITH SUCCINIC ACID AND PYRIDINE

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A new mixed-ligand complex $\{[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O\}_n$ was synthesized via the interaction of equimolar amounts of cobalt nitrate and sodium succinate in the presence of pyridine at pH 5.5–6.0. The complex was investigated by X-ray structure analysis, elemental analysis, UV/VIS and IR spectroscopies, and differential thermal analysis. The complex is a one-dimensional coordination polymer and crystallizes in the orthorhombic space group Pbca with unit cell parameters a=11.8945 Å, b=8.9064 Å, c=15.1116 Å, $\alpha=\beta=\gamma=90^0$. The atom of cobalt has a slightly distorted octahedral N_2O_4 environment and forms Co–N bonds with two molecules of pyridine and Co–O bonds with the carboxyl groups of two symmetric succinic acid molecules. The coordination number Co(II) is supplemented up to 6 by two water molecules, which are located in the axial plane of the coordination polyhedron. Due to the monodentate coordination of two symmetrically independent carboxylate oxygen atoms of one succinic acid molecule, one-dimensional coordination polymer chains are formed. Polymer chains in the crystal are united by intermolecular hydrogen bonds, which leads to the formation of layers packed in the crystal parallel to the (001) plane. Hirschfeld surface analysis and two-dimensional fingerprint plots were used to analyze the intermolecular interactions present in the crystal.

Keywords: mixed-ligand complexes; cobalt; succinic acid; pyridine; crystal structure.

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