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Photochemical Decarboxylation and Deacetylation of the Cobalt(III) Aminocarboxylate Complexes: The Crystal Structure of the $[Co(CH_2CH_2CH_2NH_2)(En)_2)]Br_2$ and $[Co(Bipy)(Cl)(Edma)]Cl \cdot 2H_2O$ Photoproducts (En is Ethylenediamine, Bipy is 2,2'-Bipyridine, and Edma is Ethylenediaminemonoacetate)

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Abstract—The crystals of $[Co(CH_2CH_2CH_2NH_2)(En)_2]Br_2$ (**I**) and $[Co(Bipy)(Cl)(Edma)]Cl \cdot 2H_2O$ (II*a*) (**IIa**) are studied by X-ray diffraction analysis. Compound **I** is synthesized by the crystallization of the $[Co(En)_2(Amb)]^{2+}$ primary photolysis products. Compound **IIa** is synthesized from the $[Co(Bipy)(Edda)]^+$ final photolysis products (En is ethylenediamine; Bipy is 2,2'-bipyridine; Edma and Edda are the anions of ethylenediaminemonoacetic and ethylenediamine-N,N'-diacetic acids, respectively; Amb is the 4-aminobutyrate ion). The crystal structure of complex **I** indicates the contraction of the seven-membered aminobutyrate $CoO_2CCH_2CH_2CH_2NH_2$ ring to the five-membered $CoCH_2CH_2CH_2NH_2$ ring by the photoelimination of the CO_2 molecule. The formation of the Co(III) complexes with the Edma ligands upon the photolysis of $[Co(Bipy)(Edda)]^+$ is due to successive reactions of contraction of the five-membered aminoacetate rings and hydrolysis of the Co–C bond.

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INTRODUCTION

An opinion that the primary photolysis process of cobalt(III) aminocarboxylates under UV irradiation in the region of ligand-to-metal charge-transfer absorption bands is the redox decomposition of the complexes to the reduced Co^{2+} ions and the ligand radicals was prevailing in the 1970s. This point of view was seemingly confirmed by the studies on the photochemistry of $[Co(Amac)_3]$ and $[Co(Edta)]^-$ [1–4] and, especially, unsuccessful attempts to find intermediate products upon pulse irradiation [3].[1] At the same time, the products preceding the redox decomposition of these complexes were found by spectrophotometry in the region of *d*–*d* transitions under the continuous irradiation of the cooled solutions [5–7]. Somewhat later these products were assumed to be the organometallic cobalt(III) compounds with the Co–C–N three-membered ring appeared after carbon dioxide was removed from the five-membred aminoacetate metalloring [8]. Further, the processes of contraction of the five- and six-membered aminocarboxylate rings in the cobalt(III) complexes to the three- or four-membered rings were proved by the X-ray diffraction analysis of the corresponding photolysis products [9–14].

The X-ray diffraction results for the $[Co(CH_2CH_2CH_2NH_2)(En)_2]Br_2$ (**I**) crystals, proving the photochemical contraction of the seven-membered aminobutyrate ring of the $[Co(En)_2(Amb)]^{2+}$ ions to the five-membered propylamine ring, are presented in this work. In addition, the routes of photolysis of the Co(III) complexes with the Edda ligands were studied, and the crystal structure of the photodeacetylation product of one of these complexes $[Co(Bipy)(Cl)(Edma)]Cl \cdot 2H_2O$ (**IIa**) was solved.

EXPERIMENTAL

Synthesis. The $[Co(CH_2CH_2CH_2NH_2)(En)_2](ClO_4)_2$ compound was synthesized by a described procedure [15]. The bromide of this cation was prepared by the

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[1] Abbreviations of the ligands: Amac, Amb, and Ala are the anions of $NH_2CH(R)CO_2^-$ amino acid, 4-aminobutyrate, and 3-aminopropionate; En, Dien, Trien, Bipy, and Phen are ethylenediamine, diethylenetriamine, triethylenetetraamine, 2,2'-bipyridine, and 1,10-phenanthroline; Edma, Edtra, Edta, Nta, Aeida, and Orntra are the anions of ethylenediaminemonoacetic, ethylene-N,N'-diacetic, ethylenediaminetriacetic, ethylenediaminetetraacetic, nitrilotriacetic, N-(2-aminoethyl)iminodiacetic, and ornithinetriacetic acids, respectively.

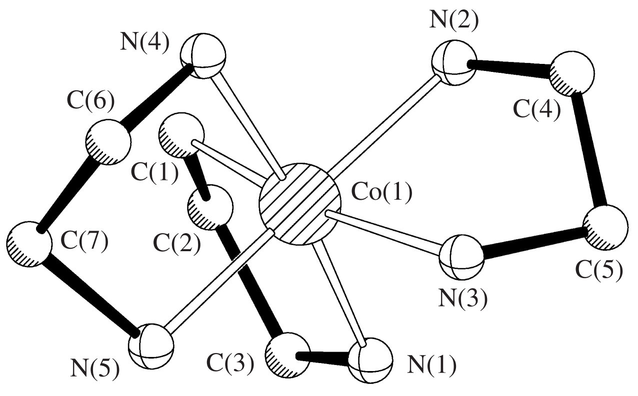


Fig. 1. One of the $[Co(CH_2CH_2CH_2NH_2)(En)_2]^{2+}$ complex cations in structure **I**. Bond lengths (Å): Co(1)–N(1), 2.01(4); Co(1)–N(2), 1.96(4); Co(1)–N(3), 2.16(4); Co(1)–N(4), 2.06(4); Co(1)–N(5), 1.94(4); Co(1)–C(1), 1.92(4).

ion exchange of a perchlorate solution on the Sephadex DEAE-25 column in the Br^- form. The crystals of compound **I** were prepared by the slow evaporation of an aqueous solution of $[Co(CH_2CH_2CH_2NH_2)(En)_2]Br_2$. Other mentioned Co(III) complexes were synthesized in the framework of previous studies according to published procedures.

Several portions (120 ml each) of an aqueous solution of *trans*(O)-[Co(Bipy)(Edda)]ClO_4 with a concentration of 10^{-3} mol/l after purging with argon were irradiated for 20 min with a DRK-120 mercury lamp and then stored for 2 h without air to complete the dark processes. Then the photolyte was acidified to pH 3 using HCl and was passed through a column packed with the Sephadex SP-25 cation-exchange resin in the Na^+ form. A minor amount of the starting complexes was eluted from the column with a solution of NaCl (0.1 M), and then two closely arranged zones were eluted with a 0.2 M NaCl solution. The first zone had the optical absorption spectrum characteristic of the low-spin Co(III) complexes with the $Co(N)_4(O)_2$ coordination mode, and the second zone contained the Co^{2+} ions. The eluate of the first zone was concentrated to a small volume on a vacuum rotary evaporator, and the remaining volume was passed through a column packed with Sephadex G-10 gel to remove NaCl. The dark red band of the photolysis products was separated on the column into two zones. The evaporation of the eluate of the first zone, which was major in volume, gave the crystals **IIa**, whose composition was determined by X-ray diffraction analysis.

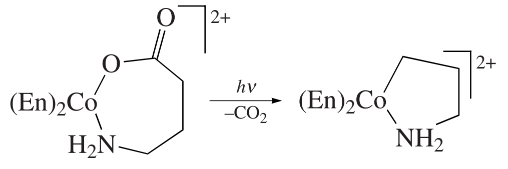
The photolysis and recording of the spectra of the frozen solutions were described [16]. A mixture of ethylene glycol and a 2 M solution of $Ba(ClO_4)_2$ (1 : 1 in volume) that vitrified at 77 K was used as a solvent.

X-ray diffraction analysis was carried out on a Siemens *P*4 automated diffractometer at room temperature. Structures **I** and **IIa** were solved by the heavy atom method and refined by the full-matrix least-squares method in the anisotropic approximation. The hydrogen atoms of the water molecules in structure **IIa** were localized in the difference Fourier syntheses, and the positions of other hydrogen atoms were geometrically calculated and refined by the riding model. All calculations were performed using the SHELXS-86 [17] and SHELXTL [18] program packages. The PLATON program was used for molecular graphics [19].

The crystallographic data, experimental details, and refinement parameters for structures **I** and **IIa** are given in Table 1. Selected bond lengths in structure **IIa** are listed in Table 2. The coordinates of non-hydrogen atoms and their equivalent temperature parameters are available from the authors.

RESULTS AND DISCUSSION

The photolysis of solutions of the $[Co(En)_2(Amb)]^{2+}$ complex in which the Amb ligand forms the seven-membered aminobutyrate ring is described [15]. The photolysis product of compound **I** was assumed to contain the five-membered ring formed due to the contraction of the seven-membered ring



(1)

(I)

This conclusion is based on an analogy of the spectral properties of compound **I** with those of the $[(En)_2Co(CH_2CH_2NH_2)]^{2+}$ cation prepared by the photolysis of $[Co(En)_2(Ala)]^{2+}$. It was reliably proved that $[Co(En)_2(CH_2CH_2NH_2)]^{2+}$ contained the four-membered ring [20]. To confirm the validity of reaction (1), the crystals of compound **I** containing the bromide ions and assumed cations **I** were studied by X-ray diffraction analysis. The determination of the structure revealed six bromine atoms in the asymmetric part of the unit cell, as well as three crystallographically independent but similar in structure complex cations, each of which, therefore, had a charge of 2+. The Co atom is coordinated by three bidentate ligands (two ligands are N,N', and the third one is N,C) that close three five-membered metallorings (Fig. 1). Just this charge and this structure of the complex should be characteristic of $[Co(En)_2(Amb)]^{2+}$ after decarboxylation via scheme (1), when the seven-membered aminobutyrate ring is contracted to the five-membered one.

The question arises: which of the six possible positions of the coordination sphere of the Co atom in each $[Co(CH_2CH_2CH_2NH_2)(En)_2]^{2+}$ cation is occupied by the donor carbon atom? The Co–C and Co–N bond lengths in the Co(III) cyclometallated complexes are similar, and the same concerns the C–C and C–N single bonds. Therefore, the question can be solved if taking into

Table 1. Crystallographic data and experimental details for structures I and IIa

Parameter	Value	
	I	II*a*
Empirical formula	$C_7H_{24}N_5Br_2Co$	$C_{14}H_{21}N_4O_4Cl_2Co$
FW	397.0	439.2
Radiation (λ, Å)	CuK_α (1.54178)	MoK_α (0.71)
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/n$
a, Å	21.9333(12)	7.721(1)
b, Å	8.7798(8)	27.333(3)
c, Å	23.4114(14)	17.621(3)
β, deg	90	99.57(1)
V, $Å^3$	4508.3	3666.9(9)
Z	12	8
ρ(calcd), g/cm^3	1.755	1.591
μ, mm^{-1}	15.12	1.253
F(000)	2376	1808
θ range, deg	2.86–26.79	1.90–22.50
Intervals of reflection indices	$-1 \le h \le 26, -1 \le k \le 10, -18 \le l \le 18$	$-1 \le h \le 8, -1 \le k \le 29, -18 \le l \le 18$
Measured reflections	5968	6577
Independent reflections, N_1	4576	4798
Number of “non-zero” reflections N_2	2015 ($I > 4\sigma(I)$), $R_{int} = 0.0746$	4798 ($I > 2\sigma(I)$), $R_{int} = 0.0273$
Number of refined parameters	181	617
Goodness-of-fit	1.875	1.054
R factors for N_2 (R_1/wR_2)	0.1506	0.0365/0.0882
R factors for N_1 (R_1/wR_2)	0.2305	0.0523/0.0974
Residual electron density (min/max) (min/max), *e* $Å^{-3}$		–0.345/0.392

account the *trans* effect of the donor C atom. For the cation shown in Fig. 1, the position of the C(1) donor atom was chosen to be in the *trans* position to the N(3) atom most remote from Co(1). However, this assignment is unreliable because of large errors in determination of the coordinates of atoms in structure **I**. It cannot be excluded that the donor carbon atoms are disordered over six possible positions of the coordination sphere in at least some of the three symmetrically independent $[Co(CH_2CH_2CH_2NH_2)(En)_2]^{2+}$ cations, and this determines the low accuracy of determination of structure **I**. The best results should be expected if, for example, a Trien molecule would be an additional ligand in the starting complex rather than two En molecules, or the polydentate ligand would contain the seven-membered ring. However, to our knowledge, no other appropriate Co(III) complexes with the seven-membered aminocarboxylate ring have not been synthesized up to now.

Table 2. Bond lengths in the cations of structure IIa

Bond	*d*, Å	
	Co(1)	Co(2)
Co–O(1)	1.898(2)	1.900(2)
Co–N(1)	1.938(3)	1.939(3)
Co–N(2)	1.929(3)	1.923(3)
Co–N(3)	1.939(3)	1.939(3)
Co–N(4)	1.946(3)	1.953(3)
Co–Cl(1)	2.259(1)	2.251(1)

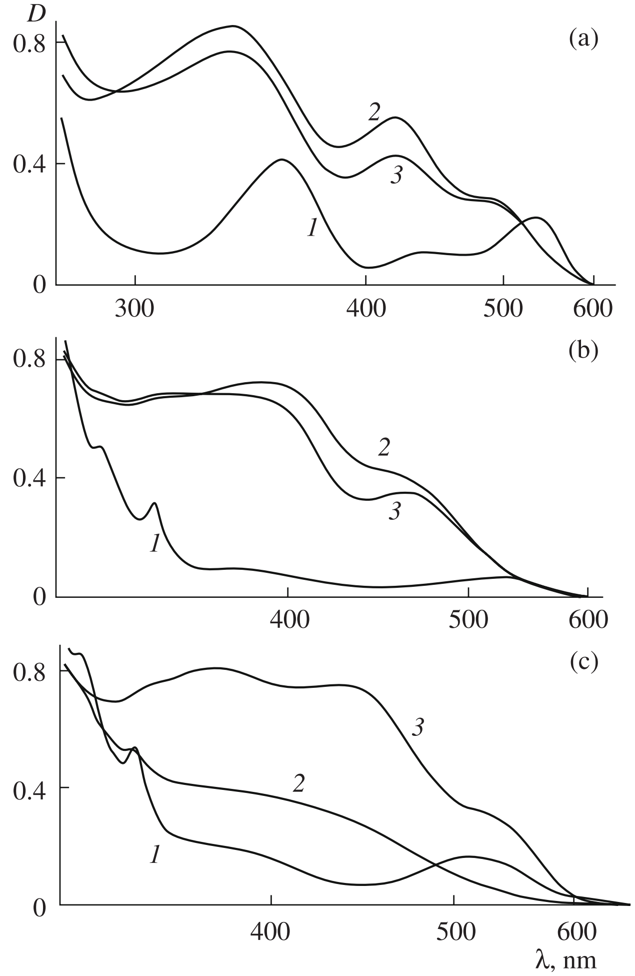
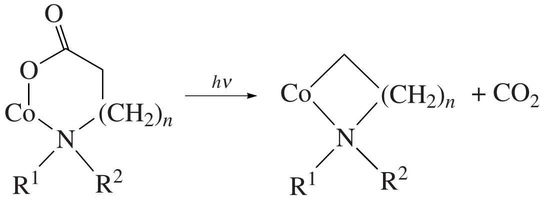


Fig. 2. Electronic absorption spectra (at 77 K) of solutions of (a) (O)-[Co(En)(Gly)$_2$]ClO$_4$, (b) *trans(*O)-[Co(Phen)(Edda)]ClO$_4$, and (c) [Co(Phen)(Nta)]: (*1*) initial solution, (*2*) after UV irradiation at 77 K, and (*3*) after short-time heating of the irradiated solution to 0°C.

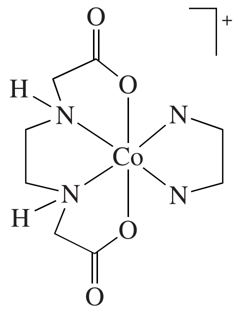
Thus, the photodecarboxylation reaction, whose particular case is the contraction of the seven-membered ring according to Eq. (1), can be written in the general form

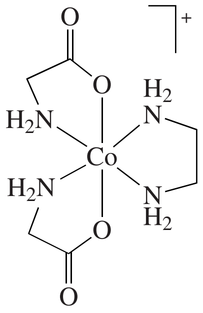


(2)

where the n parameter determining the size of the chelate rings is 0, 1, or 2; R^1 and R^2 are the hydrogen atoms or other substituents that can contain donor atoms, including carboxy groups. Then, reaction (1) corresponds to the case of $n = 2$.

The [Co(N–N)(Edda)]$^+$ (**III**) and [Co(En)(Gly)$_2$]$^+$ (**IV**) complexes considered below





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(**IIIa–IIIc**: N–N = Bipy (*a*), Phen (*b*), En (*c*)) (**IV**)

contain the *trans*-Co(N)$_4$(O)$_2$ tetragonally distorted chromophore and, hence, their spectra can exhibit three absorption bands in the visible and near-UV regions. According to the ligand field theory, two long-wavelength bands correspond to the *d–d* transitions from the $^1A_1$ ground state to the ^1E and $^1A_2$ sublevels of the $^1T_1$ state split by the tetragonal field, and the short-wavelength band corresponds to the weakly split $^1T_2$ state [21]. Let us designate these bands in the indicated order as B1, B2, and B3, and the corresponding wavelengths will be designated as λ_1, λ_2, and λ_3. In the *trans*-Co(N)$_4$(O)$_2$ octahedral chromophore of complexes **III** and **IV**, the apical positions are occupied by the donor O atoms of the carboxy groups creating a weaker field compared to that created by the N atoms in the equatorial plane. For similar complexes, $\lambda_1 < \lambda_2$ [21]. For instance, in the electronic spectrum of compound **IV**, the B2 band is observed at 532 nm, B1 is observed at 450 nm [22], and the splitting increases with the temperature decrease to 77 K (Fig. 2a, curve *1*). An analogous pattern is observed for compound **IIIc** [23]. In the case of the **IIIa** and **IIIb** ions, $\lambda_2 = 540$ nm ($\varepsilon = 120$ l mol^{-1} cm^{-1}), and B1 band is poorly seen and appears as a smooth short-wavelength slope of the B2 band [24]. The B3 short-wavelength *d–d* band at 380 nm of complexes **IIIa** and **IIIb** is partially disguised by the beginning intrinsic absorption of the Bipy or Phen ligands (Fig. 2b, curve *1*).

The product of reaction (2) at $n = 0$ is the cobalt(III) complex with the Co–C bond in the three-membered ring with a CCoN angle of 42°–44° [12–14, 20]. Since the contribution of the Co–C bond to the inner-crystalline field appreciably exceeds the contribution of the Co–N bond, the crystalline field of the photodecarboxylation product should have a strong axial component, regardless of the number of other O and N atoms in the coordination sphere of the Co atom. Therefore, it should be expected that the absorption spectrum of the product in the region of *d–d* transitions will be three-component with the arrangement of the B1 and B2 bands determined by the condition $\lambda_2 < \lambda_1$. This assumption (first advanced in [8]) is justified experimentally. For instance, the spectrum of photodecarbox-

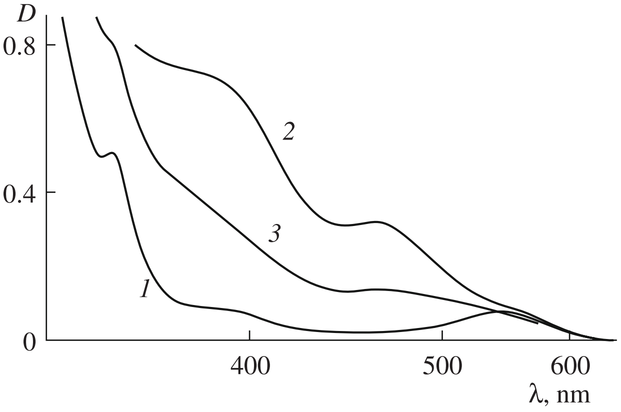


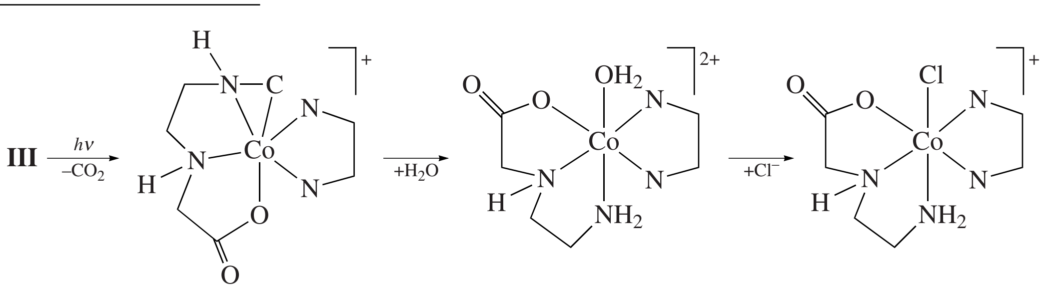
Fig. 3. Electronic absorption spectra of an aqueous solution of *trans*-[Co(Phen)(Edda)]ClO$_4$ (*1*) at room temperature, (*2*) after UV irradiation for 1 min, and (*3*) after 23 min.

ylation product **IIIc** isolated in solution using ion-exchange chromatography [25] exhibits the B2 band at 432 nm ($\varepsilon = 140$ l mol^{-1} cm^{-1}), the B1 band as a shoulder at 500 nm ($\varepsilon = 120$ l mol^{-1} cm^{-1}), and B3 at 338 nm ($\varepsilon = 300$ l mol^{-1} cm^{-1}). An analogous pattern of the *d–d* bands of the photodecarboxylation product in a liquid solution was obtained for the [Co(En)$_2$(Amac)]$^{2+}$, [Co(Trien)(Amac)]$^{2+}$ [26, 27], and [Co(Orntra)]$^-$ complexes [28].

In the case of a low stability of the product of reaction (2), it is natural to decrease the temperature, for example, using liquid nitrogen. The UV irradiation of solutions of compound **IV** frozen at 77 K induces the replacement of three bands of the starting complexes (Fig. 2a, curve *1*) by three new bands (Fig. 2a, curve *2*). After the starting complexes transformed almost completely, the relatively slow photodecomposition of the primary photolysis products becomes noticeable. Spectra *2* (Fig. 2b and 2c) were recorded approximately at the moment when the photoinduced absorbance reached a maximum. The shape of spectrum *2* in Fig. 2a corresponds to the product with the three-membered ring: the B3 and B2 bands are the maxima at 337 and 420 nm, respectively; and B1 is the shoulder at ~490 nm. The heating of the irradiated solution to the liquid state does not substantially changes the spectrum (curve *3*). The earlier studied behavior of solutions of compound **IIIc** is similar. The photolysis of a frozen solution of compound **IIIc** is illustrated by Fig. 2b. Unlike compounds **IIIc** and **IV**, the B2 (460 nm) and B3 (absorption in a broad region at 380 nm) bands of photolysis product **IIIb** are highly intense. For instance, ε for the maximum at 460 nm in curve *3* is at least 600 l mol^{-1} cm^{-1}, if the literature value ($\varepsilon = 120$ l mol^{-1} cm^{-1}) is accepted for the maximum at 540 nm in curve *1*. The B1 low-intensity band of the product should be equated to the smooth slope in curves *2* and *3* in a region of $\lambda > 530$ nm.

The considered cases with complexes **IIIb** and **IV** show that reaction (2) at $n = 0$ also occurs in the rigid glassy matrix at 77 K. This is indicated by experiments with the [Co(En)$_2$(Amac)]$^{2+}$ and [Co(Amac)$_3$] complexes, as well with [Co(Edta)]$^-$ and similar complexes [8, 16]. However, a different mechanism can also take place. For instance, if a solution of [Co(Phen)(Nta)] is irradiated at 15°C, a band at 454 nm with a shoulder at 520 nm appears, and its intensity is several times higher than that of the $1^1A_1 \longrightarrow {}^1T_1$ band (532 nm) of the starting complexes. The absorption curve for the solution irradiated at 77 K has no pronounced bands, and instead the absorption increases monotonically with a decrease in the wavelength (Fig. 2c, curve *2*). If the same solution is heated to 0°C, three bands characteristic of the Co–C–N ring appear (curve *3*). All these data imply the following. Although in a rigid matrix a CO$_2$ molecule detaches from the [Co(Phen)(Nta)] complex, the Co–C bond is not formed because of steric hindrance, but the so-called "radical pair" is stabilized as the Co(II) complex with the Phen molecule and the $^\bullet$CH$_2$NR$_2$ radical, which is a residue of the Nta ligand ($R = CH_2CO_2^-$). As the glassy matrix softens, the Co–C bond closes, showing the transition to spectrum *3* (Fig. 2b).

The photodecarboxylation product of complex **IIIb** formed in the first step of transformations **III** $\longrightarrow$ **V** at room temperature disappears with a half-life time of ~15 min, which can be judged by a decrease in the intensity of its bands at 460 and 380 nm (Fig. 3, curves *2, 3*). As mentioned in Experimental, the Co^{2+}



(3)

(**V**) (**VI**) (**II**)

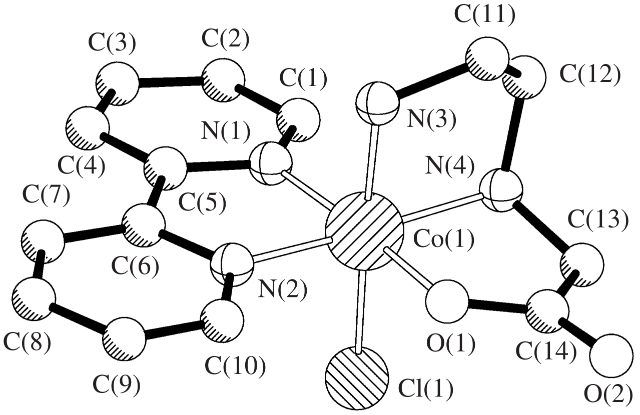


Fig. 4. One of the $[Co(Bipy)Cl(Edma)]^+$ complex cations in structure **IIa**.

ions and new Co(III) complexes are observed in the aged solution of compound **IIIa**. The new Co(III) complexes were isolated from the photolyte as two-charge cations **VIa** by ion-exchange chromatography with chloride ions. After the eluate was purified and concentrated by evaporation, crystals of the chloride of one-charge complex cation **IIa** were formed. As shown by X-ray diffraction analysis, the asymmetric part of crystals **IIa** contain four molecules of water of crystallization, two isolated chloride ions, and two complex cations, which are built similarly. Each cation contains the bidentate Bipy molecule (Fig. 4). There is an additional tridentate ligand containing eight non-hydrogen atoms and forming two conjugated five-membered rings with the Co atom. Undoubtedly, this is the residue of the Edda ligand (ethylenediaminemonoacetate ion, $H_2NCH_2CH_2NHCH_2CO_2^-$) bound to the central Co atom, the N(3) and N(4) atoms, and the O(1) atom of the carboxy group. Finally, the octahedral environment of the Co atom is completed by the monoatomic ligand, which is identified as the chloride ion by the electron density value. Thus, the composition of crystals **IIa** is expressed by the $[Co(Bipy)(Cl)(Edma)]Cl \cdot 2H_2O$ formula, which means, first of all, the loss of one acetate group compared to the starting complex **IIIa**.

The Co–O and Co–N bond lengths in structure **IIa** (Table 2) are close to the values found earlier for other Co(III) complexes with the Edma ligand [29, 30]. In the related $[Co(Bipy)(Dien)(Cl)]Cl_2 \cdot 3H_2O$ complex [31], the Co–N (1.944–1.951(4) Å) and Co–Cl (2.263(2) Å) bond lengths are close to the corresponding values for complex **IIa**.

The formation of complex **IIa** can be explained by the hydrolytic cleavage of the Co–C bond in decarboxylation product **Va**, due to which the CH_2 group is removed as a small molecule (perhaps, CH_3OH) and stable complex **VIa** is formed. Complex **VIa** was eluted from the chromatographic column as chloride. The concentrating of the eluate is accompanied by the anation: the insertion of the chloride ion into the coordination sphere of the Co(III) (scheme 3), and the crystals of compound **IIa** precipitate.

It could be assumed that the redox decomposition products of complexes **III** oxidized by air oxygen serve as the source of compounds **VI** and **II**. However, this explanation is not valid, because the photolysis was carried out in an inert atmosphere and the photolyte was acidified prior to contact with atmosphere, which prevents oxidation. Totally, the sequence of transformations **III** $\longrightarrow$ **V** $\longrightarrow$ **VI** in scheme (3) implies the loss of the acetate group. Therefore, the appearance of complexes **VI** after the excitation of the ligand-to-metal electron transfer should be named photodeacetylation.

In complex **IIa**, the Cl^- ion is localized in the *trans* position to the N atom (without the acetate group) of the Edma ligand. This situation cannot be a result of the simple removal of the carboxy and CH_2 group of any aminoacetate ring of complexes **III**. Therefore, the geometric isomerization that occurs in the transition from **III** to **VI** is required. Photodeacetylation was observed for the first time for the $[Co(Edta)]^-$ complexes [32]. It turned out that three geometric isomers of $[Co(Edtra)(H_2O)]$ are formed. The isomer with the *trans* arrangement of the acetate groups at the same N atom cannot be synthesized by the simple removal of one of the two nonequivalent acetate groups (axial or equatorial) of the starting $[Co(Edta)]^-$ complex [33]. The $[Co(Edta)(CN)]^{2-}$ complex undergoes photodeacetylation in a yield of 96% [33]. This means that only the solvent (H_2O molecules) rather another complex particle is the reactant on going from the decarboxylated to deacetylated product. It should be assumed that the same concerns the photolysis of the complexes with the Edda ligand.

In the present work, the labile photolysis products were obtained in frozen solutions, which made it possible to use stationary spectrophotometry to detect the products. An alternative is flash photolysis in combination with fast detection methods. This approach was used [3] when studying $[Co(Edta)]^-$, but no short-lived photolysis products were observed. We showed [7, 8] for the frozen solutions of the most part of the Co(III) aminocarboxylates that the primary photolysis products possessed no considerable absorption in the region between the short-wave *d–d* band and the charge-transfer band. Therefore, the mentioned negative result [3] is natural. However, we found further that the photodecarboxylation products with the intense (ε was to 6000 l mol^{-1} cm^{-1}) absorption bands in the near-UV region were formed in neutral solutions of some complexes, for instance, $[Co(Edta)(CN)_2]^{3-}$ [34], $[Co(En)(Aeida)]^+$, and $[Co(En)(Nta)]$. It would be interesting to study the flash photolysis of these rather available complexes to determine the kinetic characteristics of the intermediate products.

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