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New Crystal Forms of Tris(2-aminoethanolato-O,N)cobalt(III): Structures and Properties

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Abstract—Crystal forms of cobalt(III) tris(2-aminoethanolate) hydrates, i.e., red cubic crystals of the composition *fac*-$[Co(NH_2CH_2CH_2O)_3] \cdot 5.44H_2O$ (*fac*-I $\cdot$ $5.44H_2O$) and blue prismatic crystals of the composition *mer*-$[Co(NH_2CH_2CH_2O)_3] \cdot 3H_2O$ (*mer*-I $\cdot$ $3H_2O$) were studied by the ^{59}Co, ^{13}C NMR and X-ray diffraction methods. It was found that *mer*-$[Co(NH_2CH_2CH_2O)_3] \cdot 3H_2O$ (*mer*-I $\cdot$ $3H_2O$) is a new pseudopolymorphic modification of *fac*-$[Co(NH_2CH_2CH_2O)_3] \cdot 3H_2O$ (*fac*-I $\cdot$ $3H_2O$), while *fac*-I $\cdot$ $3H_2O$ represents a new polymorphic modification of the complex *mer*-$[Co(NH_2CH_2CH_2O)_3] \cdot 3H_2O$ (*mer*-I $\cdot$ $3H_2O$) described previously. The comparative analysis of the spectra revealed dynamic equilibrium between these geometric isomers; the *fac*-isomer is stable in aqueous solutions.

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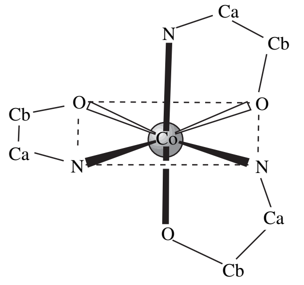
Octahedral metal complexes with N,O-bidentate ligands can give both geometric isomers and isomers with different chirality, polymorphic modifications, and complexes with different number of solvate molecules (pseudopolymorphism). On the other hand, compounds of this type can form geometric isomers with facial (***fac***) and meridional (***mer***) positions of donor groups of the same sort. Therefore, the mechanism of intermolecular interactions in crystals can show principal changes.

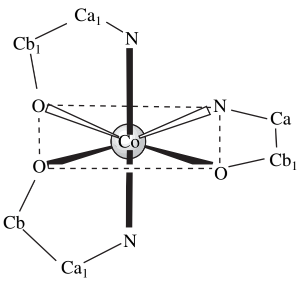
The first data on the synthesis of tris(2-aminoethanolato-O,N)cobalt(III) trihydrate, $[Co(NH_2C_2H_4O)_3] \cdot 3H_2O$ (**I · 3H$_2$O**), were published in [1]. Later [2–4], it was shown that under specific conditions, compound I $\cdot$ $3H_2O$ also crystallized as pentahydrate. At the same time, the author of [3] reported that crystals of two form simultaneously precipitated from an aqueous solution of I $\cdot$ $3H_2O$, namely, crystals of red–violet and violet–blue color. These two forms were assumed to be the *fac*- and *mer*-isomers of compound I $\cdot$ $3H_2O$. Later [5], we confirmed this assumption when studying aqueous solutions of I $\cdot$ $3H_2O$ by the ^{59}C NMR method and examining crystals of a red–violet form by X-ray diffraction method. It was concluded that the red–violet form should be assigned to the *fac*- and the violet–blue form, to the *mer*-isomer. Note that the O atoms in the structure of *fac*-I $\cdot$ $3H_2O$ ($a = b = 14.668(7)$, $c = 4.955(3)$ Å, space groups $R3$) [6] are statistically ordered over two positions such that the crystal can be presented as a product of cocrystallization of two equally probable polyhedral isomers with octahedral and trigonal-prismatic coordination of the Co atom.

The meridional form of this compound, i.e., *mer*-I $\cdot$ $3H_2O$, was also studied by X-ray diffraction method ($a = 19.871(4)$, $b = 8.8510(18)$, $c = 14.660(3)$ Å, $\beta = 134.39(3)°$, space group $C2$) [7]. In the structure of *mer*-I $\cdot$ $3H_2O$, as in *fac*-I $\cdot$ $3H_2O$ [5], the disordering in the metal coordination sphere was observed, with octahedral coordination of the Co atom remaining unchanged. Today, the Cambridge Structural Database contains data on the structures of six Co(III) compounds with monoethanolamine or its deprotonated forms. The structure of $[Co(NH_2C_2H_4O)(NH_2C_2H_4OH)_2][Co(NH_2C_2H_4O)_2 \times (NH_2C_2H_4OH)] \cdot 3ClO_4 \cdot 0.5H_2O$ was determined three times.

The aim of this work was to study the structure of two crystal form of cobalt(III) tris(2-aminoethanolate): *fac*-$[Co(NH_2C_2H_4O)_3] \cdot 5.44H_2O$ (***fac*-I · 5.44H$_2$O**), pseudopolymorphic modification of the compound *fac*-I $\cdot$ $3H_2O$ described in [2, 6] as a new pentahydrate form, and *mer*-$[Co(NH_2C_2H_4O)_3] \cdot 3H_2O$ (***mer*-I · 3H$_2$O**), which is a new polymorphic modification of a complex investigated in [7].



fac-Isomer



mer-Isomer

EXPERIMENTAL

Reagent grade cobalt chloride and monoethanolamine were used in the synthesis.

The complex *fac*-I · 5.44H_2O was obtained as a result of recrystallization of Co(III) tris(β-aminoethanolate) trihydrate synthesized by the known procedure [4]. The starting complex (2 g) was dissolved in minimum water amount with slight heating. The solution pH was increased to 10.5 with concentrated KOH solution. The obtained solution was heated on a water bath for 5–10 min at 60°C and filtered off. On slow evaporation of the solution at room temperature for 3–4 days, red–violet cubic crystals precipitated.

Table 1. Crystallographic characteristics and parameters of *fac*-I · 5.44H_2O and *mer*-I · 3H_2O

Parameter	Value	
	fac-I · 5.44H_2O	*mer*-I · 3H_2O
Empirical formula	$C_6H_{28.88}CoN_3O_{8.44}$	$C_6H_{24}CoN_3O_6$
M	337.13	293.21
Crystal system	Cubic	Rhombic
Space group	$I43d$	$Pna2_1$
a, Å	22.783(3)	10.0540(2)
b, Å	22.783(3)	6.6530(2)
c, Å	22.783(3)	13.7800(4)
V, Å^3	11826(2)	1198.82(5)
Z	32	4
T, K	150	150
Crystal size, mm	0.24 × 0.18 × 0.12	0.20 × 0.20 × 0.15
ρ(calcd.), g/cm^3	1.515	1.625
μ_{Mo}, mm^{-1}	1.199	1.451
Range of angles, deg	2.83–25.97	2.78–25.98
Number of measured reflections	38596	8188
Number of independent reflections, $I < 2\sigma(I)$	1931 (R_{int} = 0.0827)	2350 (R_{int} = 0.0305)
Number of refined parameters	115	145
Absolute structural parameter	0.05(3)	–0.018(18)
Δρ(max) and Δρ(min), *e*Å^{-3}	0.359 and –0.261	0.672 and –0.416
GOOF on F^2	1.025	1.070
R, *wR** ($I > 2\sigma(I)$)	0.0510, 0.1044	0.0259, 0.0692

$$^*wR = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}.$$

For *fac*-[Co($NH_2C_2H_4O$)$_3$] · 5.44H_2O

anal. calcd. (%):	Co 17.51,	N 12.46.
Found (%):	Co 17.24,	N 12.52.

The complex *mer*-I · 3H_2O was synthesized similarly, but the reaction was performed in more alkaline medium (pH 11–12) in order to stabilize the *mer*-isomer [5]; the reaction mixture was heated at 70°C for 15–20 min. The precipitated crystals had blue-violet color.

For *mer*-[Co($NH_2C_2H_4O$)$_3$] · 3H_2O

anal. calcd. (%):	Co 20.10,	N 14.33.
Found (%):	Co 19.87,	N 14.12.

X-ray diffraction analysis. The experimental intensities for both complexes were measured at 150 K on a Nonius Kappa CCD diffractometer (MoK_α radiation, graphite monochromator). The crystal–detector distance was 40 mm. The orientation matrix and the unit cell parameters were obtained from reflections of the first 10 frames and refined for all experimental set of the data. The peak integration and the Lorentz and polarization corrections were introduced with DENZO program [8], the intensity calibration and refinement of crystal parameters were performed with SKALEPACK program. The *fac*-I · 5.44H_2O and *mer*-I · 3H_2O structures were solved by the direct methods and refined in anisotropic approximation for all non-hydrogen atoms (SHELX97) [9]. The positions of all H atoms were located from the Fourier difference synthesis, their isotropic thermal parameters were taken as 1.2U_{eq} of the corresponding C, N, and O atoms.

Crystallographic characteristics of the title complexes and the main parameters of the structure refinement are given in Table 1.

The NMR spectra were recorded on a BRUKER AC-400 spectrometer with $K_3[Co(CN)_6]$ and TNS used as standards while recording the ^{59}Co and ^{13}C NMR spectra, respectively. D_2O was used as a solvent.

RESULTS AND DISCUSSION

The comparison of the data in Table 1 with the data published in [6, 7] makes it possible to conclude that both isomers, i.e., *mer*- and *fac*-I · 3H_2O, crystallize in both chiral and achiral space groups. The stereospecific

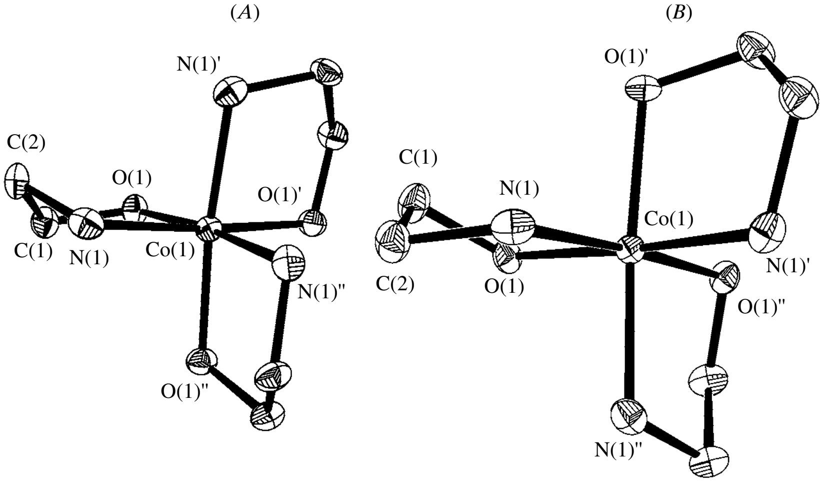


Fig. 1. Molecular structure of complexes $[Co(NH_2C_2H_4O)_3]$ (*A* and *B*) in *fac*-I · $5.44H_2O$.

synthesis is likely to be determined by the thermal factor and pH of an aqueous solution of the complex. Note that in the cases of the optically active crystals *fac*-I · $3H_2O$ [6] and *mer*-I · $3H_2O$ [7], the disordering in the first coordination sphere of Co is observed. This can be determined by tendency toward twinning in the case of chiral space groups of a crystal.

According to X-ray diffraction data, the *fac*-I · $5.44H_2O$ crystal belongs to cubic crystal system with two asymmetric complexes $[Co(NH_2C_2H_4O)_3]$ (***A***, ***B***) in independent part. Their molecular structure is represented in Fig. 1, the bond lengths are listed in Table 2. Both Co atoms occupy partial positions on threefold axis. Therefore, the crystal contains tris(complexes) of different chirality and thus, is racemate. Every Co atom is surrounded by three organic ligands forming slightly distorted octahedron where every three O and N atoms lie in common face. The average value of the chelate OCoN angle is 86.1(2)°. The five-membered metal rings have *gauche*-configuration with the C atoms deviating from the CoNO plane by –0.372 (C(1)), +0.315 (C(2)), and +0.143 (C(1)), –0.508 Å (C(2)) for molecules *A* and *B*, respectively. The parameters of the Co coordination polyhedron and ligand in two structures under study are close to those previously established for *fac*-I · $3H_2O$ [6]. The key role in crystal structure is played by hydrogen bonds N–H···O and O–H···O (Table 3). The former bonds unite the molecules of *fac*-$[Co(NH_2C_2H_4O)_3]$ into chains such that each Co octahedral complex in Co(1*A*)···Co(1*B*)···Co(1*A*)···Co(1*B*) is simultaneously a donor and acceptor of hydrogen bonds (Fig. 2) (Co(1*A*)···Co(1*B*) 4.903(1) Å). The chains are packed in a crystal along threefold axis. The O–H···O hydrogen bonds involving solvate H_2O molecules join infinite chains into a three-dimensional framework. The projection of crystal structure of *fac*-I · $5.44H_2O$ along threefold axis is shown in Fig. 3. The atoms O(1*w*) and O(5*w*) lie on fourfold axis.

In meridional isomer *mer*-I · $3H_2O$, the central Co atom also retains its octahedral configuration (Fig. 4). The average distances Co–N 1.951, Co–O 1.914 Å (Table 2) are close to analogous distances found in disordered polymorphic modification described in [7] (Co–N 1.94, Co–O 1.90 Å). There is no essential difference in the distances Co–N (to the N atoms in the *trans*-positions relative to the O atoms) as compared to the distances in the N–Co–N chains. The comparison of the Co–N and Co–O bond lengths in *mer*-I · $3H_2O$ with the values determined for the *fac*- I · $3H_2O$ modification [6] does not indicate mutual influence of location of the donor groups on the metal–ligand distance either. The

Table 2. Bond lengths (*d*) in *fac*-I · $5.44H_2O$ and *mer*-I · $3H_2O$

Bond	*d*, Å (complex *A*)	*d*, Å (complex *B*)
fac-I · $5.44H_2O$		
Co(1)–O(1)	1.936(3)	1.931(3)
Co(1)–N(1)	1.962(4)	1.947(4)
O(1)–C(1)	1.406(6)	1.411(5)
C(1)–C(2)	1.526(7)	1.530(7)

Bond	*d*, Å	Bond	*d*, Å
mer-I · $3H_2O$			
Co(1)–O(1)	1.919(2)	Co(1)–N(2)	1.945(3)
Co(1)–N(1)	1.948(2)	Co(1)–N(3)	1.957(2)
O(1)–C(1)	1.414(4)	O(2)–C(3)	1.416(3)
O(3)–C(5)	1.416(4)	N(1)–C(2)	1.483(4)
N(2)–C(4)	1.468(4)	N(3)–C(6)	1.494(3)
C(1)–C(2)	1.517(4)	C(3)–C(4)	1.519(4)
C(5)–C(6)	1.510(4)		

Table 3. Characteristics of hydrogen bonds in structures *fac*-I · 5.44H_2O and *mer*-I · 3H_2O

D–H···A	Distance, Å			DHA angle, deg	Transformation of atom A
	D–H, Å	H···A, Å	D···A, Å		
fac-I · 5.44H_2O					
N(1*A*)–H···O(1*B*)	0.90	2.05	2.892(5)	156	1.5 – *z*, *x*, 1 – *y*
N(1*B*)–H···O(1*A*)	0.90	2.05	2.917(5)	162	1.75 – *x*, 1.25 – *z*, 0.25 + *y*
O(1*w*)–H···O(2*w*)	0.97	1.93	2.889(4)	173	*x*, *y*, *z*
O(3*w*)–H···O(2*w*)	0.96	1.87	2.813(6)	167	*x*, *y*, *z*
O(3*w*)–H···O(1*A*)	0.96	1.79	2.624(6)	144	*x*, *y*, *z*
O(4*w*)–H···O(3*w*)	0.96	1.80	2.712(7)	158	*x*, *y*, *z*
O(5*w*)–H···O(4*w*)	0.83	1.94	2.763(5)	171	*x*, *y*, *z*
O(2*w*)–H···O(1*B*)	0.91	1.81	2.691(5)	163	*x*, *y*, *z*
O(2*w*)–H···O(4*w*)	0.91	1.94	2.823(6)	164	1.75 – *x*, 1.25 – *z*, 0.25 + *y*
mer-I · 3H_2O					
N(1)–H···O(1)	0.90	1.96	2.829(3)	163	*x* – 1/2, –*y* + 1/2, *z*
N(2)–H···O(3)	0.90	2.12	2.947(3)	153	*x* + 1/2, –*y* + 1/2, *z*
N(3)–H···O(2)	0.90	1.97	2.864(3)	173	*x* + 1/2, –*y* + 1/2, *z*
O(1*w*)–H···O(1)	0.89	1.88	2.748(3)	163	
O(1*w*)–H···O(2*w*)	0.89	1.87	2.709(4)	159	*x* + 1/2, –*y* – 1/ 2, *z*
O(2*w*)–H···O(3*w*)	0.96	2.11	3.048(4)	166	–*x* + 1, –*y*, *z* – 1/2
O(2*w*)–H···O(2)	0.90	1.92	2.706(3)	144	
O(3*w*)–H···O(1*w*)	0.89	1.87	2.742(4)	163	–*x* + 1, –*y*, *z* + 1/2
O(3*w*)–H···O(3)	0.90	1.86	2.711(3)	157	

same tendency of chain formation from neutral Co complexes linked by hydrogen bonds can be seen in the packing (Fig. 5). The geometric parameters of hydrogen bonds for *mer*- I · 3H_2O are also listed in Table 3. The difference from the *fac*-isomer consists in that in each unit of the chain, the complex acts twice as a donor and once as an acceptor of hydrogen bonds. Such a difference is specified by topology of the donor and acceptor groups of the complex. The chains are packed in parallel to the *x*-axis of the crystal. The space between the chains is occupied by solvate H_2O molecules united by the O–H···O_L and N–H···O_w hydrogen bonds into 3D framework.

In the case of the red–violet modification *fac*-I · 5.44H_2O, the ^{59}Co NMR spectrum contains one signal with the chemical shift 10175 ppm. The ^{59}Co NMR spectrum of freshly prepared aqueous solution (pH > 10) of the blue-violet modification *mer*-I · 3H_2O (Fig. 6) exhibits two signals with the chemical shifts 10175 and 10016 ppm (against $[^{59}Co(CN)_6]^{3-}$). A signal with $\delta(^{59}Co) = 10016$ ppm was assigned to the *mer*-isomer, while the other signal with $\delta(^{59}Co) = 10175$ ppm,

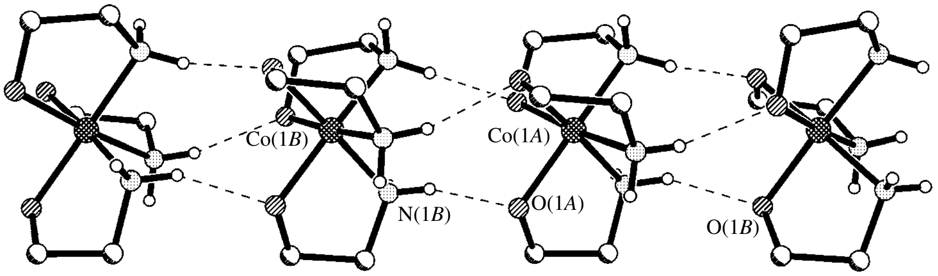


Fig. 2. The molecular complexes $[Co(NH_2C_2H_4O)_3]$ united in a chain by the N–H···O hydrogen bonds in *fac*-I · 5.44H_2O crystal.

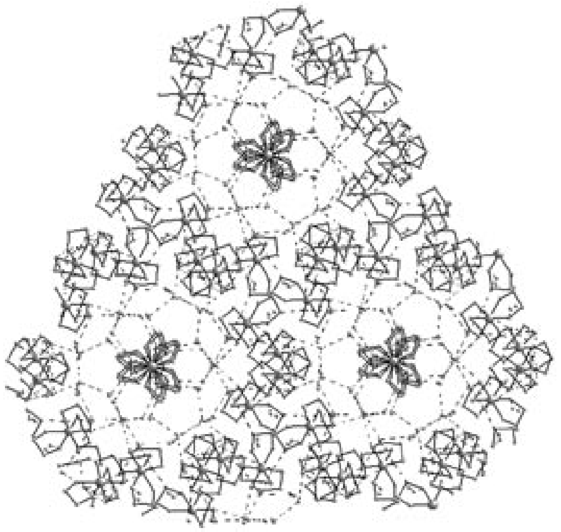


Fig. 3. Projection of crystal structure of *fac*-I · $5.44H_2O$ along axis 3.

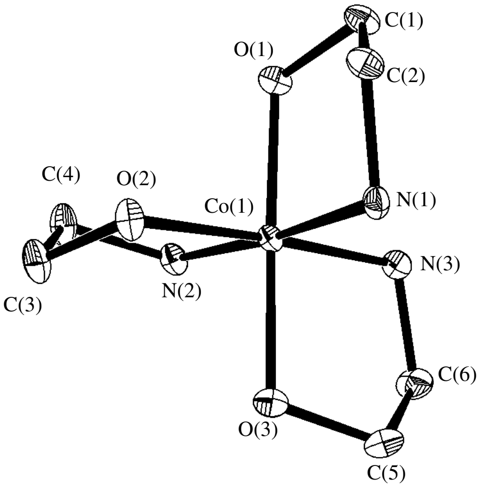


Fig. 4. The structure of the $[Co(NH_2C_2H_4O)_3]$ complex in the *mer*-I · $3H_2O$ crystal.

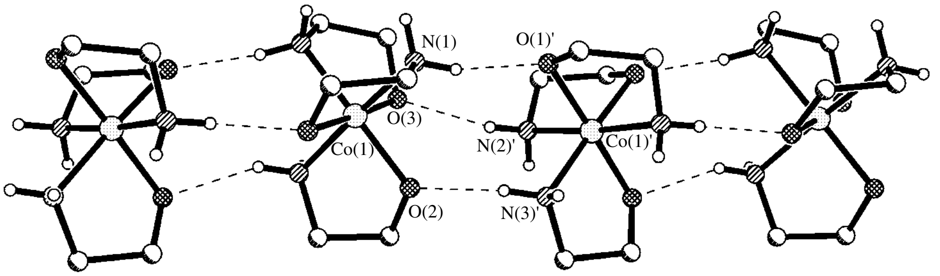


Fig. 5. The $[Co(NH_2C_2H_4O)_3]$ complexes linked into a chain in the *mer*-I · $3H_2O$ crystal.

to the *fac*-isomer of $[Co(NH_2C_2H_4O)_3]$. Therefore, the isomerization process *mer* ⟶ *fac* starts immediately after dissolution, unlike the reverse process *fac* ⟶ *mer*, which occurs much slower and only in the presence of the hydroxide ions. Further study of the spectral changes with time showed that the intensity of a signal corresponding to the *fac*-form increases, while the intensity of a signal from the *mer*-isomer decreases and it disappears completely. Thus, the NMR study we performed confirms that in aqueous solutions, $[Co(NH_2C_2H_4O)_3]$ occurs as a stable *fac*-isomer.

The ^{59}Co NMR spectra of *fac*- and *mer*-$[Co(NH_2CH_2CH_2OH)_3]Cl_3$ obtained from hydrochloric acid solutions and the spectrum of acidified solution of *fac*- and *mer*-$[Co(NH_2CH_2CH_2O)_3]$ are identical (Table 4). Hence, the CoN_3O_3 coordination core for Co is not disturbed, while the upfield shift of the ^{59}Co NMR signals by ~600 ppm can be explained by protonation of coordinated amino alcohol and the formation of the cationic complex

$$[Co(OCH_2CH_2NH_2)_3] + 3H^+ \longrightarrow [Co(HOCH_2CH_2NH_2)_3]^{3+}.$$

In the study of the *mer* ⟶ *fac* kinetics, the starting complex concentration was 0.01 mol/l. In such a dilute solution, the concentration of water molecules can be considered constant. The equilibrium concentrations of *mer*- and *fac*-$[Co(NH_2CH_2CH_2O)_3]$ were determined by the ^{59}Co NMR spectra by integrating the surface areas corresponding to the signals. Since the function $\log c_{mer}$–τ is linear, the first order in the *mer*-isomer was suggested for isomerization reaction. The rate con-

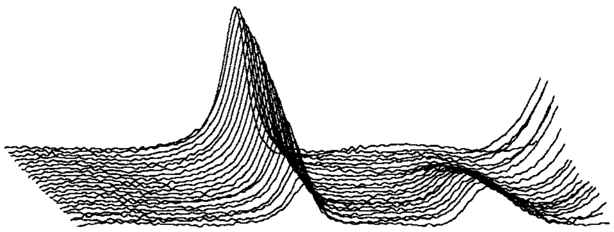


Fig. 6. The ^{59}Co NMR spectrum of an aqueous solution of *mer*-I · $3H_2O$.

Table 4. The chemical shifts (against $[Co(CN)_6]^{3-}$ and width of ^{59}Co NMR lines

Compound	$\delta(^{59}Co)$, ppm	$\Delta H/2$, Hz
mer-$[Co(OCH_2CH_2NH_2)_3] \cdot 3H_2O$ (blue–violet)	10016	1350
fac-$[Co(OCH_2CH_2NH_2)_3] \cdot 3H_2O$ (red–violet)	10175	1250
mer-$[Co(OCH_2CH_2NH_2)_3] \cdot 3H_2O$ + + H^+ (blue–violet)	9455	3000
fac-$[Co(OCH_2CH_2NH_2)_3] \cdot 3H_2O$ + + H^+ (red–violet)	9575	1500
mer-$[Co(OCH_2CH_2NH_2)_3]Cl_3$ (blue–violet)	9425	2900
fac-$[Co(OCH_2CH_2NH_2)_3]Cl_3$ (red–violet)	9590	1290

Table 5. Rate constant of *mer* ⟶ *fac* isomerizaiton $K \times 10^4$ and activation energies E_a

T, K	K, s^{-1}	E_a, kJ/mol
289	1.92 ± 0.05	50.28
299	5.02 ± 0.05	
309	11.20 ± 0.05	

stants calculated for isomerization reaction *mer* ⟶ *fac* at different temperatures are given in Table 5. The activation energy (***E****a*) of this process (50.28 kJ/mol) was found from the slope of $\log K–1/T$.

The mechanism of the *fac* ⟶ *mer* isomerization described in [10] suggests the formation of intermediate complex with 2N + 4O surrounding of the central Co atom. It was shown in [11] that the transformation *mer* ⟶ *fac* occurs due to rotation of the Co coordination polyhedron about axis 3 as trigonal or rhombic twist. The trigonal twist results in the formation of the optical Δ-*fac*- and Λ-*fac*-isomers, while the rhombic twist gives the Δ-*fac*- and Λ-*mer*-isomers.

The ^{13}C NMR spectrum of blue-colored crystals (Fig. 7) contains six signals, which also indicates two isomers in a solution. The *mer*-$[Co(OCH_2CH_2NH_2)_3] \cdot 3H_2O$ corresponds to four groups of nonequivalent C atoms in the Co coordination polyhedron: CN(N, OO, NO); CN (O, OO, NN); CO (N, OO, NN), and CO (O, ON, NN). Two different groups of C atoms occur in the *fac*-isomer: CN (O, NO, NO) and CO (N, NO, NO), which were assigned as follows: 44.92 ppm—*fac*-CN (O, NO, NO); 43.78 ppm—*mer*-CN (N, OO, NO); 43.85 ppm—*mer*-CN (O, OO, NN); 62.47 ppm—*fac*-CO (N, NO, NO); 62.18 ppm—*mer*-CO (N, OO, NN); 61.95 ppm – *mer*-CO (O, ON, NN).

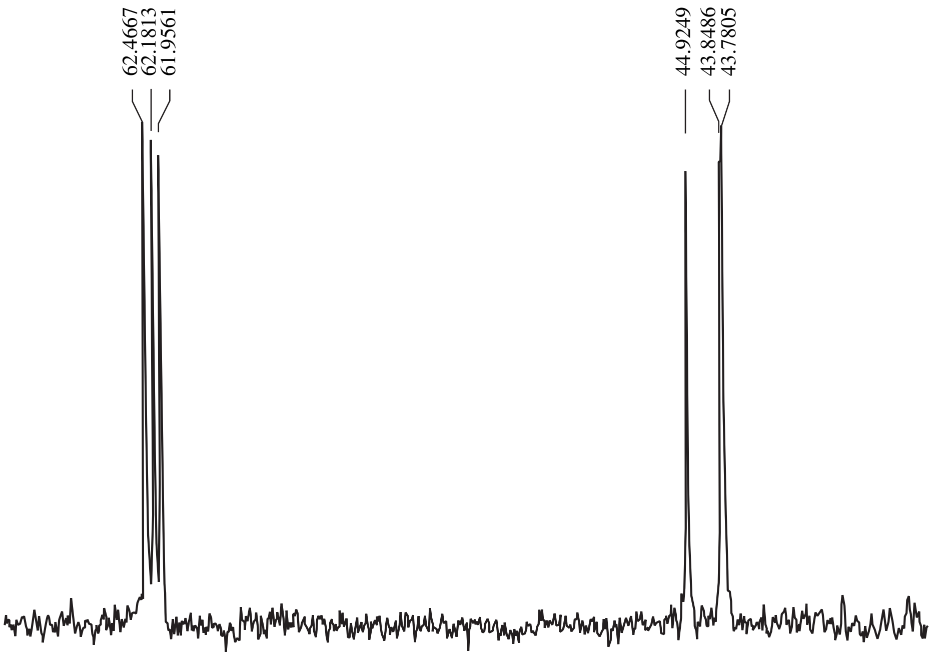


Fig. 7. The ^{13}C NMR spectrum (σ, ppm) of an aqueous solution of *mer*-I · $3H_2O$.

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