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JAHN–TELLER EFFECT IN THE $[CuEn_3]CrO_4$ STRUCTURE

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A change in the coordination of the copper atom in the crystal structure of $[CuEn_3]CrO_4$ (En is ethylenediamine) in studied in the range 150-300 K. According to the single crystal X-ray diffraction (XRD) data at 150 K, the single crystal has a complicated twining character based on the triclinic cell ($a = 9.027(2)$ Å, $b = 13.335(3)$ Å, $c = 13.339(3)$ Å, $\alpha = 71.77(3)°$, $\beta = 70.53(3)°$, $\gamma = 70.42(3)°$) composed of two crystallographically independent $[CuEn_3]^{2+}$ complex cations. The coordination of copper atoms is a distorted square bipyramid; four short Cu–N distances lie in the range 2.049-2.082 Å; two long ones are 2.415 Å and 2.470 Å. According to the differential scanning calorimetry (DSC) data, near 218 K there is a phase transition. The single crystal XRD experiment performed at 250 K ($a = 15.6992(19)$ Å, $c = 9.7573(13)$ Å, $V = 2082.6(6)$ Å^3, space group $P\bar{3}c1$ (No. 165), $Z = 6$) shows that chromate anions are disordered over three positions about the c axis, and Cu–N distances are 2.120-2.177 Å. According to the DSC data, on further heating the structure undergoes yet another two alterations (260 K and 270 K) due to the disordering of oxygen atoms of chromate anions and the subsequent equalization of Cu–N distances. At 300 K in the structure ($a = 9.0778(6)$ Å, $c = 9.7715(5)$ Å, $V = 697.4$ Å^3, space group $P\bar{3}1c$ (No. 163), $Z = 2$) all Cu–N distances are 2.155 Å, and chromate anions are disordered over six positions about the c axis. A comparative crystal chemical analysis of the packing of the studied structures is carried out.

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A large number of works have been dedicated to the study of the Jahn–Teller effect in Cu(II) complexes. Among the complex cations in which this effect was observed, the most known are: $[Cu(H_2O)_6]^{2+}$, $[Cu(bpy)_3]^{2+}$, $[Cu(phen)_3]^{2+}$, $[Cu(OMPA)_3]^{2+}$ (OMPA is octamethylpyrophosphoroamide), and $[CuEn_3]^{2+}$. This work is concerned just with the latter. In [1] the synthesis of $[CuEn_3]SO_4$ and $[CuEn_3]SO_4{\cdot}H_2O$ was described and IR data were given. The structure of $[CuEn_3]SO_4$ has been repeatedly studied [2-4]; at 120 K it is triclinic, and the difference in Cu–N distances (further, Δ) is 0.17 Å. According to [5], at 110 K $\Delta \sim 0.33$ Å. Even a larger Δ value of 0.50 Å was determined in the structure of $[CuEn_3]Cl_2 0.75En$ (space group $C2/c$) [4]. In [6] it is shown that at 180 K the structure of $[CuEn_3]SO_4$ is hexagonal (space group $P\bar{3}$, No. 147), with all the Cu–N distances being equivalent and the Jahn–Teller effect being absent. Features of the change in the thermal vibrations of atoms and their disorder in the temperature range 190-270 K were explored in [7]. It is shown that on heating $[CuEn_3]SO_4$ the equivalent Cu–N distances increase insignificantly: from 2.1473(18) Å to 2.1495(19) Å. It seems interesting

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to investigate the Jahn–Teller effect in other complex salts involving $[CuEn_3]^{2+}$. This work is devoted to the elaboration of the synthesis procedure and the structural study of $[CuEn_3]CrO_4$ in a wide temperature range.

EXPERIMENTAL

Synthesis. Complex salt was obtained by the interaction of freshly precipitated $Cu(OH)_2$ with ethylenediamine in the presence of a target anion. In the work, $Cu(NO_3)_2{\cdot}3H_2O$ (chemically pure), ethylene hydrate (analytical grade), and K_2CrO_4 (chemically pure) were used. Copper(II) hydroxide was prepared by adding an aqueous NaOH solution to an aqueous copper nitrate solution to pH 11.0. To this end, 1 mmol of $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in 15 ml of H_2O and 3 ml of a 1 M NaOH solution in H_2O was added. The reaction mixture was stirred and freshly precipitated $Cu(OH)_2$ was centrifuged at 2000 rpm for two minutes. The precipitate was four times washed with a water-alcohol mixture (30 ml ethanol: 70 ml H_2O) in 25 ml portions on a centrifuge. Freshly precipitated $Cu(OH)_2$ and washed from the traces of unreacted NaOH and $NaNO_3$ was dissolved in En in the equivalent ratio Cu(II):En = 1:3. Upon dissolution a dark blue liquid phase formed. The phase was kept for 20-30 min at room temperature and 1 mmol of K_2CrO_4 dissolved in 4 ml of H_2O was transferred into it. The reaction mixture was stirred and put into a desiccator above solid alkali. On the second day, green (emerald) coarse crystal phase precipitated from the solution. The phase was filtered off, washed with methanol, and dried in the air.

The IR spectrum (Fig. 1) was measured on a Scimitar FTS 2000 (Bruker) instrument in the wavelength range 400-4000 cm^{-1} in KBr pellets. The band assignment was made using the literature data [8, 9]. In the region of stretching vibrations of the N–H bond two intense absorption bands are observed with the maxima at 3219 cm^{-1} and 3099 cm^{-1}, which are characteristic of antisymmetric and symmetric stretching vibration of the NH_2 group of coordinated ethylenediamine. According to the literature data [8], in the free ethylenediamine molecule, vibrational bands of NH_2 groups are observed at 3400 cm^{-1} and 3325 cm^{-1} respectively.

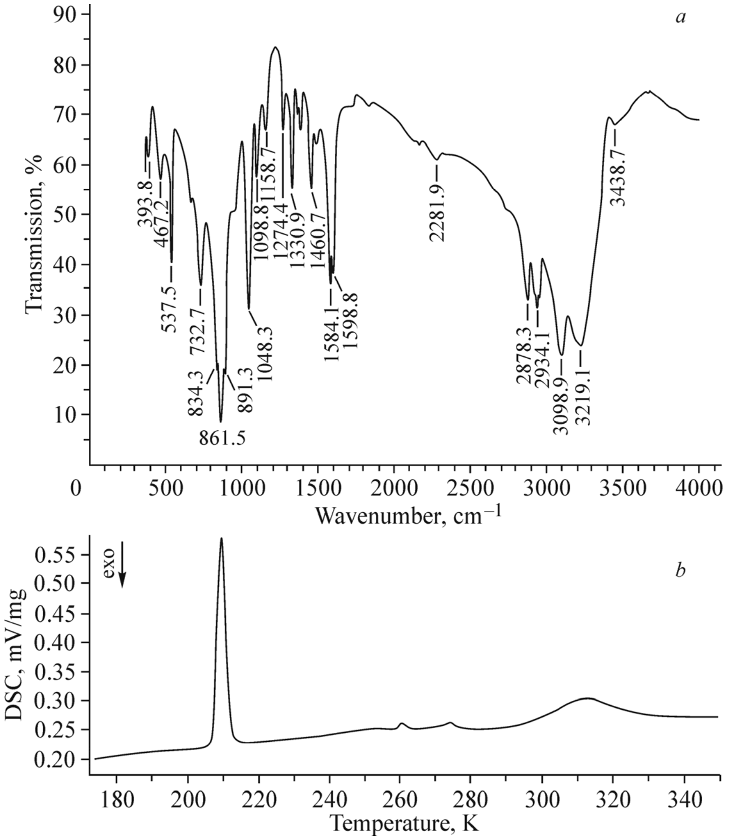

Fig. 1. IR spectrum (*a*) and DSC curve (*b*) for $[CuEn_3]CrO_4$.

To examine the thermodynamic properties a NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter was used. The heat flow sensor and the temperature scale were calibrated by melting the reference substances (C_6H_{12}, $C_{10}H_{16}$, Hg, Ga, $C_{10}H_8$, C_6H_5COOH, In). To enhance the sensitivity and diminish the basic line noise the measurements were carried out with a heating rate of 9 K/min without liquid nitrogen supply (calorimeter cell heating rate ~8 K/min at 150 K). DSC measurements of the sample (10-12 single crystals) were carried out by a heat flow technique at a constant heating rate in a non-hermetic aluminum crucible with a lid in a 25 ml/min Ar flow in the temperature range from 150 K to 350 K. The basic line signal obtained on heating of two empty crucibles was subtracted from the experimental results. The obtained curve is shown in Fig. 1*b*.

The powder XRD study was performed on a SHIMADZU XRD-7000 diffractometer (CuK_α radiation, Ni filter, scintillation detector with amplitude discrimination) at room temperature. The sample was deposited in a thin layer on the polished side of the standard cuvette. A Si sample (SRM-640c) prepared similarly was used as the external reference. Initially, the diffraction pattern was indexed using the single crystal XRD data on $[CuEn_3]SO_4$ [6] and it was found that the phases were isostructural. The final refinement was made using the PCW program [10] based on the single crystal XRD data at 300 K. No “excess” lines were detected in the XRD pattern of the freshly synthesized sample, which indicated that it was single-phase. On storing in the air the sample became moist in a day, and lines of $[CuEn_2CrO_4]_n$ appeared in the XRD pattern [11, 12 No. 1564364]. Already in two days, the sample completely represented this phase. The same phase formed as a result of performing DSC (heating in the Ar flow to 500 K). One of the single crystals subjected to heating was analyzed on a BRUKER APEX DUO diffractometer (CuK_α radiation, two-dimensional detector, room temperature) by the procedure [13]: the obtained XRD pattern totally corresponds to the theoretical XRD pattern of $[CuEn_2CrO_4]_n$ [11; 12 No. 1564364].

XRD analysis of a single crystal (hexagonal green prism with the dimensions 0.2×0.2×0.2 mm) was conducted on an automated Bruker DUO diffractometer (MoK_α radiation, graphite monochromator, APEX II CCD detector) at 150 K, 250 K, and 300 K. The measurement strategy employed standard φ- and ω-scans with a width of 0.5°. Primary integration, absorption correction, and global refinement of UCPs were made using the Bruker APEX2 V2013.6-2 program package (SAINT V8.32B, SADABS-2012/1, and TWINABS-2012/1) [14]. Crystallographic data are summarized in Table 1. The obtained data sets were processed with Olex2 1.2 [15] using the SHELXT-2014/5 program [16] for the primary structure solution by a direct method and SHELXL-2017/1 [17] for the subsequent refinement. The analysis of a single crystal at 150 K shows a complicated twining character: all the selected crystals consist of three pairs of partially overlapping crystal domains where each pair of domains is related by a –1 0 0/0 0 –1/0 –1 0 twining matrix and has totally overlapping diffraction spots, while all three pairs intergrow with a 120° turn about the [–1 1 1] direction. This causes the formation of a pseudo-hexagonal superlattice ($a = 17.95$ Å, $c = 19.54$ Å, $V = 5451$ Å^3), in which the reflections in $hk(2n)$ planes belong to each of the six domains, and in the $hk(2n+1)$ planes, 1/3 of diffraction peaks belong to each pair of domains. Such a complicated twining is completely similar to the situation described in [5], and seems to be due to that on passing from the hexagonal structure (250 K) to the triclinic one (150 K) based on two crystallographically independent complex $[CuEn_3]^{2+}$ cations there are six equally probable positions. All atoms (except hydrogen atoms) were refined in the anisotropic approximation. Hydrogen atoms were located by the residual electron density peaks and refined in the isotropic approximation using the riding model: N–H 0.89 Å and C–H 0.97 Å. It is established that the structure corresponds to $[CuEn_3]CrO_4$ complex salt – $C_6H_{24}CrCuN_6O_4$. The formula unit weight is 359.85 arb. u. Atomic coordinates and thermal parameters have been deposited with CCDC [12] and can be obtained at www.ccdc.cam.ac.uk/data_request/cif. The main geometric characteristics of the complex cations and chromate anions are listed in Table 1.

RESULTS AND DISCUSSION

150 K. In two crystallographically independent complex cations the CuN_6 coordination cores represent distorted (4+2) bipyramids with four short and two long Cu–N distances. The geometric characteristics of the coordination cores are listed in Table 1 and Fig. 2. The short Cu–N distances are in the range 2.049-2.082 Å and long ones are within 2.415-

TABLE 1. Results of the Refinement of the Crystal Structure of [CuEn$_3$]CrO$_4$

Temperature, K	150	250	300
a, Å; α, deg	9.0268(18); 71.77(3)	15.6992(19)	9.0778(6)
b, Å; β, deg	13.335(3); 70.53(3)	15.6992(19)	9.0778(6)
c, Å; γ, deg	13.339(3); 70.42(3)	9.7573(13)	9.7715(5)
V, Å^3	1389.2(6)	2082.6(6)	697.35(10)
Space group	$P\bar{1}$ (No. 2)	$P\bar{3}c1$ (No. 165)	$P\bar{3}1c$ (No. 163)
Z; V/Z, Å^3	4; 347.3	6; 347.1	2; 348.7
ρ_{calc}, g/cm^3	1.721	1.721	1.714
μ, mm^{-1}	2.330	2.331	2.321
F(000)	748	1122.0	374.0
2θ range data collection, deg	3.324-56.57	2.996-61.01	5.182-66.178
$N_{meas.}$ / $N_{indep.}$	10793 / 9161	22505 / 2131	2292 / 828
$R_{integr.}$ / $S(F^2)$	0.0348 / 1.078	0.0233 / 1.049	0.0177 / 1.078
Data collection completion (2θ ≤ 50°), %	100	100	99.3
N of refined parameters	330	119	59
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0296 / 0.0738	0.0293 / 0.0823	0.0256 / 0.0648
R_1 / wR_2 (all data)	0.0389 / 0.0773	0.0512 / 0.1002	0.0327 / 0.0696
∠N–Cu–N, deg	78.9. 82.9. 79.1*	79.65. 80.86(×2)	80.27(×3)
Cu–N, Å	2.434(5), 2.064(6) 2.043(6), 2.057(6) 2.077(6), 2.454(5)	2.120 (×2) 2.160 (×2) 2.177 (×2)	2.155(2) (×6)
N–C, Å	1.458-1.505	1.469, 1.477	1.471
C–C, Å	1.513-1.546	1.506, 1.509	1.499
∠Cu–N–C, deg	100.8-111.8	108.1-109.0	108.4
∠N–C–C, deg	106.4-111.7	108.3, 108.6	108.5
Δ, Å**	–0.266 / 0.455 –0.473 / 0.239 –0.337 / 0.427	–0.367 / 0.352 –0.364 / 0.364	–0.362 / 0.362
Cr–O, Å	1.616(5)-1.670(4)	1.578(10)-1.639(4)	1.604(14), 1.622(16)
∠O–Cr–O, deg	108.3-112.7	108.4-110.7	101.1-115.3
No. CCDC	1576939	1576937	1576938

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* Geometric characteristics of the second complex cation are given in Fig. 2.

** Deviations of carbon atoms from the plane of the N–Cu–N triangle. For the second complex cation: –0.381 / 0.347; –0.339 / 0.402; –0.371 / 0.345.

2.470 Å. Nearly the same situation was observed in the structure of [CuEn$_3$]SO$_4$ at 120 K [5, 9 TENCUS11]: short Cu–N distances of 2.046-2.073 Å and long ones of 2.373-2.395 Å. As seen, in our case, the values of long distances are noticeably larger. The largest ∠N–Cu–N values (82.9° and 84.4°) are observed in the "symmetric" ligands, i.e. with both short Cu–N distances. In the "asymmetric" ligands they are 78.9-80.0°. In the structure of [CuEn$_3$]SO$_4$ at 120 K [5] the angles are 83.57° and 84.37° in the "symmetric" ligands against 79.66-80.42° in the "asymmetric" ones. All ligands have the *gauche* configuration: the carbon atoms deviate from the planes of N–Cu–N triangles to different sides.

The structure contains two crystallographically independent chromate anions. The Cr–O distances are in the range 1.616(5)-1.670(4) Å, and ∠O–Cr–O is within 108.4-110.7°.

The analysis of the general structural motif is conducted by the procedure [18], based on the number of formula units per unit cell (i.e. $Z = 4$). The theoretical XRD pattern was calculated only with respect to copper atoms. The application

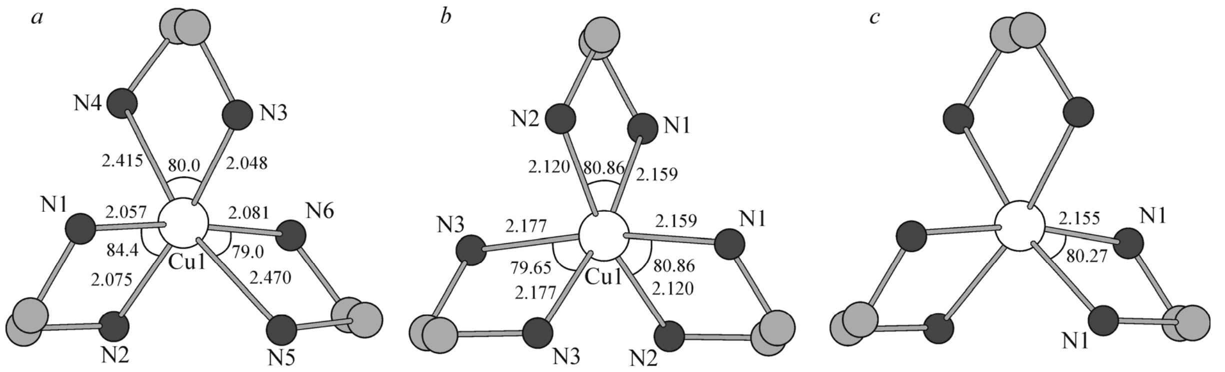

Fig. 2. Changes in the geometric characteristics of the coordination core of the complex $[\mathrm{CuEn}_3]^{2+}$ cation with increasing temperature: 150 K (characteristics of CA involving Cu2 are given in Table 1) (*a*), 250 K (*b*), 300 K (*c*). H atoms are not shown.

of this approach to a number of similar cases was described in [19-23]. The calculated intense reflections indicate the planes mostly occupied by particular atoms, copper atoms, in our case. Then, by means of the program [24], triples for which the matrix composed of *hkl* indices has a determinant equal to the number *Z* were distinguished among these planes. The most

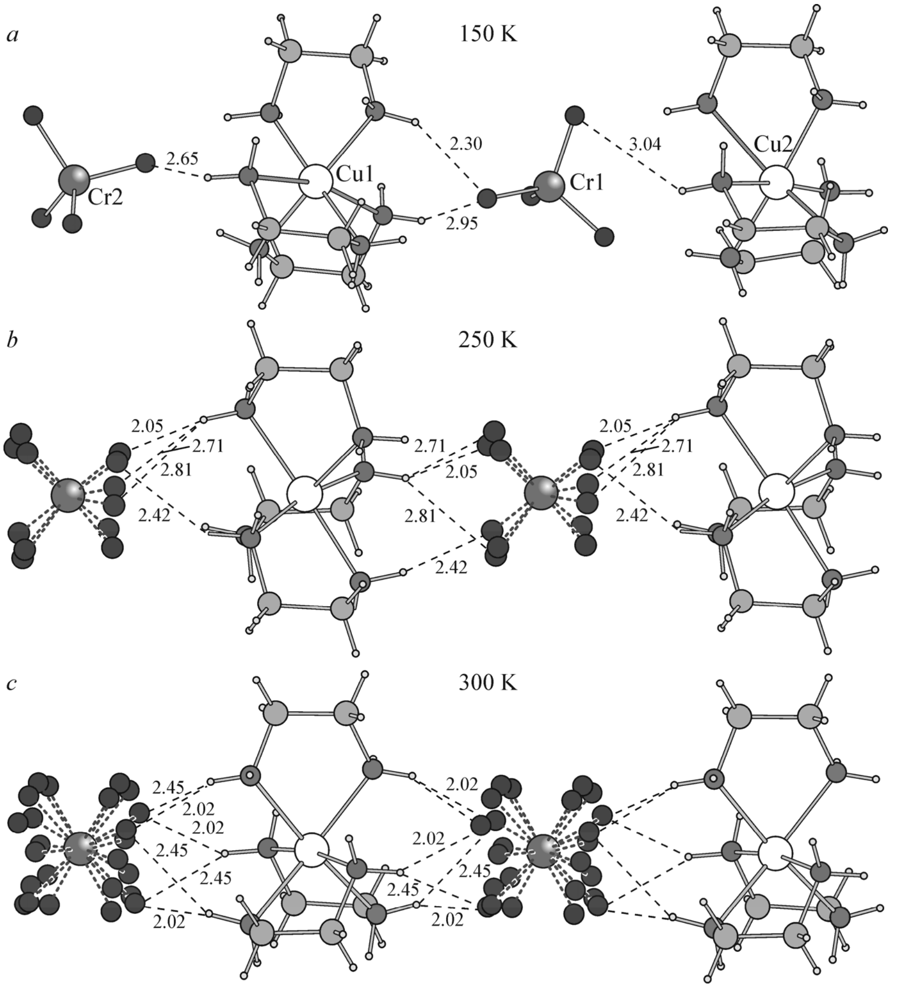

Fig. 3. Changes in the geometry of interionic N–H…O contacts in cation–anion chains with increasing temperature: 150 K (*a*), 250 K (*b*), 300 K (*c*) (contacts <2.5 Å are shown). Interatomic distances to the disordered oxygen atoms are shown by dashed lines.

symmetric sublattice was chosen among the variants. Finally, the sublattice formed by the intersection of three families of crystallographic planes with (1 1 0) and (0 1 –1), (0 2 2) indices was found. The copper atoms follow the sites of this sublattice. The subcell parameters are: $a_T = 9.03$ Å, $b_T = 9.02$ Å, $c_T = 4.92$ Å, $\alpha_T = 89.89$, $\beta_T = 90.33$, $\gamma_T = 119.94°$. They allow us to consider the structure as pseudo-hexagonal in the $\boldsymbol{c}_T$ direction (Fig. 2). This vector can be expressed through unit cell vectors as $\boldsymbol{c}_T = -\boldsymbol{a}/4 + \boldsymbol{b}/4 + \boldsymbol{c}/4$. Two other vectors are: $\boldsymbol{a}_T = \boldsymbol{a}/2$ and $\boldsymbol{b}_T = -\boldsymbol{a}/2 + \boldsymbol{b}/2 - \boldsymbol{c}/2$.

It is convenient to describe the mutual arrangement of the ions as the packing of cation…anion… chains (Fig. 3*a*) along the distinguished pseudo-hexagonal direction $\boldsymbol{c}_T$ (Fig. 4*a*). Distances in the chain are: Cr(2)…Cu(1) 5.12 Å, Cu(1)…Cr(1) 4.98 Å, Cr(1)…Cu(2) 4.85 Å; ∠ Cr(2)…Cu(1)…Cr(1) 179.1°, ∠Cu(1)…Cr(1)…Cu(2) 176.7°. The shortest N–H…O contacts are 2.30 Å; the contacts between the ions from the neighboring chains have the same values. In the layer (Fig. 4*a*) the Cr…Cu distances are in the range 5.04-5.98 Å and the angles are 115.2-123.8°.

In the temperature dependence of the DSC signal (Fig. 1*b*) (the range from 150 K to 250 K) an endothermal peak is observed at $T_{\text{onset}} = 207.2$ K. This endothermal peak is due to the structural phase transition caused by the Jahn–Teller distortion of the local environment of the Cu(II) ion. As the repeated experiments show, the transition is reversible.

250 K. According to the single crystal XRD data, the heating of the single crystal from 150 K to 250 K resulted in the transition from the triclinic symmetry to hexagonal ($P\bar{3}c1$, No. 165). The complex cations became equivalent together with the Cu–N distances (Δ does not exceed 0.057 Å). The ∠N–Cu–N angles are 79.65° and 80.86°. For comparison, at a similar temperature the characteristics of the complex cation in the structure of $[\text{CuEn}_3]\text{SO}_4$ [5; 9 TENCUS05] are: Δ = 0.001 Å, angle difference ∠N–Cu–N 0.03°.

Chromate anions are disordered over three positions, the average value of Cr–O distances having slightly decreased: from 1.644 Å to 1.612 Å. The structure of cation…anion… chains is shown in Fig. 3*b*. All the Cr…Cu distances are 4.88 Å,

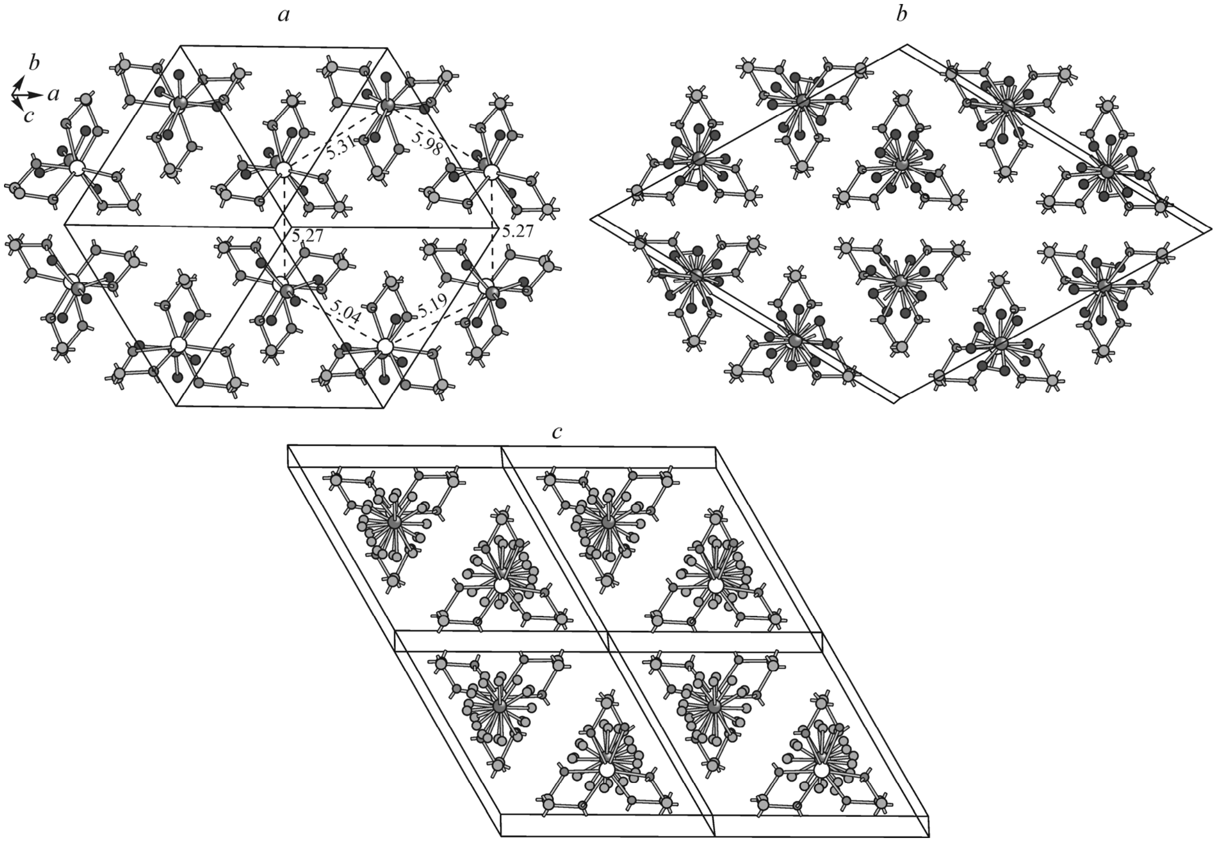

Fig. 4. Projections of crystal structures of $[\text{CuEn}_3]\text{CrO}_4$ at different temperatures: 150 (*a*), 250 (*b*), 300 K (*c*). H atoms are omitted.

and ∠Cr…Cu…Cr is 179.95°. The shortest N–H…O contacts are 2.05 Å in the chains and 2.27 Å between the neighboring chains (Fig. 4*b*).

In the temperature range from 250 K to 300 K two thermal anomalies are observed at 259.3 K and 272 K, which are caused by the disordering of oxygen atoms of chromate anions and a subsequent alignment of the Cu–N distances.

300 K. The transition to the $P\overline{3}1c$ space group (No. 163) is accompanied by the final equalization of the Cu–N, ∠N–Cu–N distances and other geometric characteristics of the complex cation. Chromate anions are disordered over six positions.

The structure of cation…anion… chains is shown in Fig. 3*c*. All the Cr…Cu distances are 4.88 Å; ∠Cr…Cu…Cr = 180°. The shortest N–H…O contacts are 2.02 Å in the chains and 1.90 Å between the neighboring chains (Fig. 4*c*).

According to the DSC data, a blurred anomaly is observed in the temperature range from 295 K to 330 K, which is likely to be due to the further disordering of chromate anions.

Thus, in this work, the synthesis of complex salt $[CuEn_3]CrO_4$ is described. It is shown that at a temperature below 207.2 K the Jahn–Teller effect is observed. The coordination of copper atoms is a distorted square bipyramid; four short Cu–N distances lie within 2.049-2.082 Å, and two long distances are 2.415 Å and 2.470 Å.

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