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Heterometallic Compounds with the Binuclear Complex Anion $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$: Synthesis and Structure

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Abstract—Heterometallic compounds $BaCr_2(OH)(Ac)(Nta)_2 \cdot 4H_2O$ (**I**) and $[Fe(L)_3][Cr_2(OH)(Ac)(Nta)_2] \cdot nH_2O$ (L is Bipy (**II**) and Phen (**III**); Bipy is α,α'-bipyridine, Phen is *o*,*o*'-phenanthroline, Ac^- is acetate ion, Nta is nitrilotriacetate ion; $n = 8$ (**II**) and 6.25 (**III**)) are synthesized. According to the X-ray diffraction data, compounds **II** and **III** have ionic structures built of the isolated complex cations $[Fe(L)_3]^{2+}$, binuclear complex anions $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$, and crystallization water molecules. The magnetic properties of compounds **II** and **III** in the interval from 2 to 300 K confirm assumptions on the diamagnetic character of $[Fe(L)_3]^{2+}$ and indicate the antiferromagnetic interaction between the chromium atoms in the dimeric fragment $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$.

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INTRODUCTION

Hydrolysis of metal ions [1, 2] plays an important role in synthetic inorganic chemistry and forms a basis for various chemical transformations involving transition metals. In particular, metal complexes are often formed due to hydrolysis [3]. As a result, polynuclear compounds are formed in which the hydroxo and oxo bridging ligands can link up to three and four metal atoms, respectively. For chromium(III) ions, these reactions afford diverse in composition and structure polynuclear compounds $\{Cr_2(OH)\}$ [4, 5], $\{Cr_2(OH)_2\}$ [6, 7], $\{Cr_3O\}$ [8–10], $\{Cr_3(OH)_2\}$ [11], $\{Cr_4O_2\}$ [12, 13], $\{Cr_4(OH)_4\}$ [14], $\{Cr_8O_4\}$, $\{Cr_8(OH)_8\}$ [15], $\{Cr_8(OH)_{12}\}$ [16], $\{Cr_{12}O_9(OH)_3\}$ [17], and $\{Cr_{12}O_{12}\}$ [18]. It has been shown earlier that the use of binuclear chromium(III) complexes is a promising method for the synthesis of complex coordination compounds because makes it possible to obtain cluster and polymeric heteronuclear structures with *s*/*d*-, *p*/*d*-, and *d*/*d* elements [19–24]. The $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$ fragment is used as a precursor capable of creating various bridging bonds through the donor oxygen atoms of the carboxy groups of the Nta^{3-} ligands [23, 24].

Continuing these works, we synthesized and studied three new compounds of this class: $BaCr_2(OH)(Ac)(Nta) \cdot 4H_2O$ (**I**), $[Fe(Bipy)_3][Cr_2(OH)(Ac)(Nta)_2] \cdot 8H_2O$ (**II**), and $[Fe(Phen)_3][Cr_2(OH)(Ac)(Nta)_2] \cdot 6.25H_2O$ (**III**), where Bipy is α,α'-bipyridine, Phen is *o*,*o*'-phenanthroline, Ac^- is acetate ion, and Nta is nitrilotriacetate ion.

EXPERIMENTAL

Synthesis of barium(I) [μ-hydroxo-μ-acetato-O,O'-bis(nitrilotriacetatochromate(III))] tetrahydrate. Water (50 ml) and glacial acetic acid (0.4 ml) were added to a mixture of H_3Nta (0.38 g, 2 mmol) and powdered $BaCO_3$ (1.18 g, 6 mmol). The mixture was heated in a water bath with stirring until the complete dissolution of $BaCO_3$. Then $CrCl_3 \cdot 6H_2O$ (0.52 g, 2 mmol) dissolved in water (15 ml) was added, and the mixture was kept for 1 h at 95°C. The violet solution formed was filtered, cooled to room temperature, and neutralized with stirring with a dilute solution of ammonia to pH 5.0. The blue-green solution was concentrated by evaporation at 60°C to 10 ml. Blue-green needle-like crystals precipitated after 24 h. The crystalline precipitate was filtered off, washed with water, alcohol, and ether, and dried at room temperature. The yield was 0.4–0.55 g (~70%).

For $C_{14}H_{24}BaCr_2N_2O_{19}$

anal. calcd, %: Cr, 13.58; Ba, 17.94; C, 21.96; H, 3.16; N, 3.66.

Found, %: Cr, 13.15; Ba, 18.00; C, 21.93; H, 3.65; N, 3.23.

UV-Vis (272–800 nm): $\lambda_1 = 406$; $\lambda_2 = 570$.

IR (KBr), cm^{-1}: 3392 m, 1624 vs, 1559 vs, 1460 m, 1381 s, 1341 m, 1208 w, 1094 m, 1006 m, 910 s, 753 s, 663 m, 614 s.

Synthesis of [trisbipyridyliron(II)] [μ-hydroxo-μ-acetato-O,O'-bis(nitrilotriacetatochromate(III))] octahydrate (II). Iron sulfate $FeSO_4 \cdot 7H_2O$ (0.278 g, 1 mmol) and α,α'-Bipy (0.32 g, 2 mmol) were added to freshly boiled, cooled, and nitrogen-saturated distilled water (25 ml). The mixture was heated at 50°C with vigorous stirring under nitrogen current. Compound **I** (0.766 g, 1 mmol) was added to the resulting intensely colored solution. The solution was stirred on heating under nitrogen current for 20–30 min, and the formed precipitate of $BaSO_4$ was filtered off. The filtrate was concentrated by evaporation at 50°C to a volume of 15 ml and cooled. Dark red crystals that precipitated during a day were washed with cold water, alcohol, and ether and dried at room temperature. The yield was 0.964 g (78%).

For $C_{44}H_{56}Cr_2FeN_8O_{23}$

anal. calcd, %:	Cr, 8.49;	Fe, 4.56;	C, 43.15;	H, 4.61;	N, 9.15.
Found, %:	Cr, 8.15;	Fe, 4.55;	C, 42.63;	H, 4.65;	N, 8.91.

UV-Vis (272–800 nm): $\lambda_1 = 299$, $\lambda_2 = 350$, $\lambda_3 = 522$.

IR (KBr) cm^{-1}: 3417 s, 3078 m, 2975 m, 1642 vs, 1602 s, 1545 s, 1464 m, 1445 s, 1428 m, 1378 vs, 1313 m, 1269 m, 1160 w, 1105 w, 1090 w, 1067 w, 1009 w, 965 w, 933 w, 911 s, 778 s, 754 m, 735 m, 668 m, 625 m, 538 m, 443 m, 422 m.

Synthesis of [trisphenanthrolineiron(II)] [μ-hydroxo-μ-acetato-O,O'-bis(nitrilotriacetatochromate(III))] hexahydrate (III). This compound was prepared analogously to compound **II** as dark red crystals with an orange shade. The yield was 1.023 g (80%).

For $C_{50}H_{52.5}Cr_2FeN_8O_{21.25}$

anal. calcd, %:	Cr, 8.22;	Fe, 4.41;	C, 47.46;	H, 4.18;	N, 8.86.
Found, %:	Cr, 8.00;	Fe, 4.54;	C, 47.02;	H, 4.36;	N, 8.80.

UV-Vis (272–800 nm): $\lambda_1 = 277$; $\lambda = 510$.

IR (KBr), cm^{-1}: 3393 s, 3054 m, 1638 vs, 1556 s, 1455 m, 1426 s, 1382 vs, 1318 m, 1270 m, 1223 w, 1143 w, 1106 w, 1094 w, 1055 w, 1011 w, 934 w, 909 s, 847 s, 780 w, 753 m, 724 s, 669 m, 619 s, 533 m, 443 m.

Compounds **I–III** are soluble in water, DMSO, and DMF and are almost insoluble in methanol, ethanol, acetone, and ether. Under normal conditions, they are stable in both crystalline and dissolved states.

IR spectra were recorded on a GX system 2000 PerkinElmer FTIR spectrophotometer. EPR spectra were measured on a Lambda 25 PerkinElmer spectrophotometer. Magnetic measurements were carried out on a Quantum Design MPMS SQUID magnetometer.

X-ray diffraction analyses of compounds **II** and **III** were carried out on a KUMA CCD diffractometer (MoK_α radiation, graphite monochromator) at 100 K. Cell determination and intensity integration were performed using the Crys Alis program package (Oxford Diffraction) [25]. The Lorentz and polarization factors were applied when recalculating from intensities to F^2. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms at the carbon atoms were calculated in the idealized positions, and their isotropic temperature parameters were determined as $1.2 \times U_{eq}$ of the corresponding C atoms. The H atoms of the H_2O molecules were found objectively and refined via the same scheme as those at the C atoms. In the both crystals the outer-sphere H_2O molecules are partially disordered, and the hydrogen atoms for them were not located.

The experimental characteristics and crystallographic data for compounds **II** and **III** are given in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The final values of the positional and thermal parameters for the compounds studied were deposited with the Cambridge Crystallographic Data Centre (CCDC, nos. 715555 (**II**) and 715556 (**III**)).

RESULTS AND DISCUSSION

Methods for the synthesis of complexes with the coordination blocks $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$ from compounds with the dimeric blocks $[Cr_2(OH)_2(Nta)_2]^{2-}$ were described [19–22]. These methods are based on the substitution of one bridging group μ-OH for μ-(O,O'-Ac) by the titration of the $[Cr_2(OH)_2(Nta)_2]^{2-}$ ion with acetic acid [20, 26].

We have previously described the methods for the preparation of the Ca and Sr compounds containing the $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$ dimeric blocks from H_3Nta, MCO_3, $CrCl_3 \cdot 6H_2O$, and CH_3COOH. The Pb and Ag complexes were obtained using the Sr salt as a precursor [26, 27].

Compounds **I–III** were synthesized in the present work via the same synthetic routes.

The IR spectra of compounds **I–III** contain doublet signals indicating different coordination modes of the carboxy groups of the Ac^- and Nta^- ligands. The characteristic absorption bands ν_{as}(C–O) and ν_s(C–O) appear in the regions 1642–1624, 156–1545 and 1382–1374, 146–1456 cm^{-1}, respectively. The value $\Delta = \nu_{as} - \nu_s$ for compounds **I–III**, which is used [28] as a criterion for the determination of a possible coordination of the carboxy groups, range from 268 to 80 cm^{-1} (Table 3). These data indicate that in compounds **I–III** the carboxy groups of Ac^- and Nta^{3-} manifest different structural functions. The Ac^- ion functions as a bidentate-bridging ligand, whereas the carboxy groups of Nta^{3-} exhibit the monodentate coordination mode.

We showed [23, 24, 26, 27] that the $[Cr_2(OH)_2(Nta)_2]^{2-}$ and $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$ anions are promising for the formation of the cluster and polymeric structures. The carboxy groups of the Nta^{3-} ligands act as organizing units for joining the dimeric fragments with the *d, f*, or *s* metal. The main condition for the formation of bridging systems in crystals is the open coordination polyhedron of the second metal. The variant of inner-sphere substitution in the second complex of one of the ligands for the oxygen atom of the carboxy group is also possible. The both variants were used in the cited works.

In the present work, we synthesized and studied two new compounds of this class in which $[FeL_3]^{2+}$ (L is Bipy (**II**), Phen (**III**)) acts as the cation. The compounds are ionic and contain no bridging system connecting the anionic and cationic fragments. It is most likely that this fact is determined by the high stability of the $[FeL_3]^{2+}$ cations. The analysis of the CCDC data [29] shows that these cations enter tens of compounds without any changes. For example, 80 works are cited for $[Fe(Bipy)_3]^{2+}$, whereas 49 works are cited for $[Fe(Phen)_3]^{2+}$.

Compound **II** (Fig. 1) is built of the complex cations $[Fe(Bipy)_3]^{2+}$, anions $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$, and the H_2O molecules in a ratio of 1 : 1 : 8. Water occupies ten crystallographic positions, four of which are pairwise distributed randomly with the 0.5 probability. The complex cation is usually octahedral with similar Fe–N distances: 1.950(5)–1.977(5) Å. For the *tris* organization of the octahedron, three metallocycles are formed with the NFeN angle equal, on the average, to 81.5° (Table 2). The structure of this structural unit is close to those observed in tris(2,2-bipyridyl)iron(III) [30–33]. In the complex dimeric anion $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$ in **II**, the Cr···Cr distance (3.482(3) Å) is close to the distances observed earlier [26]. Each Cr atom has octahedral coordination due to the N and 3O atoms (Nta^{3-}) and the O atoms of the bridging OH group and the residue of acetic acid as a *syn–syn*-bridging ligand. The interatomic distances in the coordination polyhedron of the chromium atom (Table 2) are also close to analogous distances [26]. The angle at the O(1) bridging atom is 130.2(2)°. Hydrogen bonds play the main role in the organization of the crystal structure. In them the H_2O molecules and the OH group of the dimer serve as proton donors in the hydrogen bonds, whereas the Nta^{3-} carboxy groups and H_2O molecules act as proton acceptors. The H_2O molecules and $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$ anions form the anionic sublattice parallel to the *xy* plane of the crystal. The space between the anionic dimeric networks is filled with the $[Fe(Bipy)_3]^{2+}$ cations.

The structure of compound **III** (Fig. 2) is basically similar to that of compound **II**. In the complex cation, the iron atom has the octahedral environment due to six N atoms of Phen. The Fe–N distances (1.960(2)–1.982(2) Å) in compound **III** are close to those found in compound **II**, and the chelate angles are close to 83.0°. As a whole, the geometry of the cation in compound **III** is close to that in the structure described [17–19]. The structure of the dimeric anion $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$ in compounds **II** and **III** is similar, as a whole, to that described earlier [26]. The Cr···Cr distance in dimer **III** is 3.490 Å, and the angle at the bridging OH group is 129.3°. The crystal structures of compounds **II** and **III** are similarly organized. The dimeric anions and H_2O molecules form the anionic sublattice due to the system of hydrogen bonds. The dimeric network is parallel to the diagonal [110]. The $[Fe(Phen)_3]^{2+}$ cations contacting with the anionic sublattice due to weak C–H···O interactions are arranged between the anionic networks.

Table 1. Crystallographic data and experimental and refinement characteristics for compounds **II** and **III**

Parameter	Value	
	II	III
FW	1224.82	1265.35
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a, Å	15.9981(12)	15.2737(6)
b, Å	13.7160(12)	15.9556(6)
c, Å	23.4683(18)	22.7438(9)
β, deg	98.780(6)	107.722(2)
V, Å^3	5089.3(7)	5279.7(4)
Z; ρ(calcd.), g/cm^3	4, 1.599	4, 1.592
μ_{Mo}, mm^{-1}	0.793	0.766
F(000)	2536	2610
θ range, deg	2.58–25.05	2.72–26.00
Index range	$-19 \le h \le 18$ $-12 \le k \le 16$ $-17 \le l \le 2$	$-18 \le h \le 18$ $-19 \le k \le 19$ $-28 \le l \le 28$
Number of measured/independent parameters	19597/8951 (R_{int} = 0.1327)	202969/10364 (R_{int} = 0.0716)
θ angle completeness, %	99.3	99.8
Number of refined parameters	701	756
Goodness-of-fit	0.980	1.043
R factor ($I > 2\sigma(I)$)	0.0535	0.0314
R factor for all reflections	0.2129	0.0441
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.435/–0.344	0.561/–0.498

The magnetic properties of compounds **II** and **III** were studied in the temperature interval 2–300 K with allowance for diamagnetic corrections [34]. The temperature dependence of the magnetic susceptibility $(\chi_M)^{-1}$ for compound **II** is shown in Fig. 3. For compound **II**, the $\chi_M T$ value at room temperature (3.56 cm^3

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the metal atoms in structures **II** and **III**

Coordination polyhedron of Cr		
Bond	*d*, Å	
	II	III
Cr(1)–O(1)	1.914(4)	1.931(1)
Cr(1)–O(8)	1.945(5)	1.964(1)
Cr(1)–O(4)	1.976(4)	1.996(1)
Cr(1)–O(6)	1.984(4)	1.946(1)
Cr(1)–O(2)	2.003(5)	1.993(1)
Cr(1)–N(1)	2.079(5)	2.063(2)
Cr(2)–O(1)	1.928(4)	1.937(1)
Cr(2)–O(14)	1.950(5)	1.937(1)
Cr(2)–O(3)	1.974(4)	1.985(1)
Cr(2)–O(12)	1.980(5)	1.985(1)
Cr(2)–O(10)	1.990(4)	1.972(1)
Cr(2)–N(2)	2.099(5)	2.070(2)
Angle	ω, deg	
	II	III
O(1)Cr(1)O(8)	90.5(2)	89.56(6)
O(1)Cr(1)O(4)	99.7(2)	101.62(6)
O(8)Cr(1)O(4)	90.51(18)	92.60(6)
O(1)Cr(1)O(6)	97.0(2)	95.08(6)
O(8)Cr(1)O(6)	90.7(2)	89.90(6)
O(4)Cr(1)O(6)	163.3(2)	163.13(6)
O(1)Cr(1)O(2)	92.8(2)	94.09(6)
O(8)Cr(1)O(2)	176.3(2)	176.34(6)
O(4)Cr(1)O(2)	87.2(2)	86.94(6)
O(6)Cr(1)O(2)	90.6(2)	89.51(6)
O(1)Cr(1)N(1)	175.2(2)	174.19(7)
O(8)Cr(1)N(1)	84.9(2)	85.20(6)
O(4)Cr(1)N(1)	81.6(2)	81.17(6)
O(6)Cr(1)N(1)	81.9(2)	82.43(6)
O(2)Cr(1)N(1)	91.9(2)	91.14(6)
O(1)Cr(2)O(14)	89.7(2)	88.46(6)
O(1)Cr(2)O(3)	92.8(2)	95.34(6)
O(14)Cr(2)O(3)	177.0(2)	176.17(6)
O(1)Cr(2)O(12)	101.4(2)	96.86(6)
O(14)Cr(2)O(12)	90.5(2)	91.07(6)
O(3)Cr(2)O(12)	87.4(2)	88.91(6)
Angle	ω, deg	
	II	III
O(1)Cr(2)O(10)	96.0(2)	99.82(6)
O(14)Cr(2)O(10)	91.7(2)	89.97(6)
O(3)Cr(2)O(10)	89.7(2)	88.95(6)
O(12)Cr(2)O(10)	162.4(2)	163.31(6)
O(1)Cr(2)N(2)	173.3(2)	172.82(7)
O(14)Cr(2)N(2)	84.3(2)	84.68(6)
O(3)Cr(2)N(2)	93.3(2)	91.53(6)
O(12)Cr(2)N(2)	81.7(2)	81.18(6)
O(10)Cr(2)N(2)	81.2(2)	82.33(6)
Coordination polyhedron of Fe		
C,flÁ¸	*d*, Å	
	II	III
Fe(1)–N(3)	1.950(5)	1.960(2)
Fe(1)–N(6)	1.960(5)	1.974(2)
Fe(1)–N(4)	1.965(5)	1.971(2)
Fe(1)–N(5)	1.973(5)	1.969(2)
Fe(1)–N(7)	1.975(5)	1.969(2)
Fe(1)–N(8)	1.977(5)	1.982(2)
Angle	ω, deg	
	II	III
N(3)Fe(1)N(6)	173.3(2)	176.33(7)
N(3)Fe(1)N(4)	81.4(2)	82.78(7)
N(6)Fe(1)N(4)	92.4(2)	94.83(7)
N(3)Fe(1)N(5)	95.7(2)	94.24(7)
N(6)Fe(1)N(5)	81.7(3)	82.91(7)
N(4)Fe(1)N(5)	91.7(2)	89.05(7)
N(3)Fe(1)N(7)	94.4(2)	94.70(7)
N(6)Fe(1)N(7)	91.9(2)	87.80(7)
N(4)Fe(1)N(7)	173.7(2)	176.34(7)
N(5)Fe(1)N(7)	93.4(2)	93.80(7)
N(3)Fe(1)N(8)	87.3(2)	90.41(7)
N(6)Fe(1)N(8)	95.8(2)	92.55(7)
N(4)Fe(1)N(8)	93.4(2)	94.29(7)
N(5)Fe(1)N(8)	174.4(2)	174.58(7)
N(7)Fe(1)N(8)	81.7(2)	83.05(7)

Table 3. IR spectral data (cm^{-1}) for compounds **I–III**

Compound	ν_{as}(C–O)		ν_s(C–O)		$\Delta = \nu_{as} - \nu_s$
	mono	bridge	mono	mono	
$BaCr_2(OH)(Ac)(Nta)_2 \cdot 4H_2O$ (I)	1624	1559	1460	1381	243 99
$[Fe(Bipy)_3][Cr_2(OH)(Ac)(Nta)] \cdot 8H_2O$ (II)	1642	1545	1464	1373	268 80
$[Fe(Phen)_3][Cr_2(OH)(Ac)(Nta)_2] \cdot 6.25H_2O$ (III)	1638	1556	1455	1382	256 100

mol^{-1} K) is close to those in other earlier studied heterometallic compounds containing the dimeric fragment with two magnetically interacting chromium atoms ($S1 = S2 = 3/2$) [23, 24, 26]. For both compounds **II** and **III** (Fig. 4) ($\chi_M T$ = 3.28 cm^3 mol^{-1} K), the magnetic properties are determined by the paramagnetic chromium dimer and the diamagnetic iron(II) cation. The analysis of the data on the basis of the Curie–Weiss law (C = 4.42(1) cm^3 mol^{-1} K), θ = –75(1) K for **II** and C = 4.38(1) cm^3 mol^{-1} K, θ = –98(1) K for **III**) confirms the assumption about the diamagnetic character of $[Fe(Bipy)_3]^{2+}$ and indicates the antiferromagnetic interaction between the chromium(III) atoms in $[Cr_2(OH)(Ac)(Nta)_2]^{2-}$.

The magnetic susceptibility was quantitatively analyzed on the basis of the classical Heisenberg–Dirac Hamiltonian $H_d = -2J\vec{S}_1\vec{S}_2$ [34–36] with allowance for paramagnetic impurities and temperature-independent paramagnetism according to the equation

$$\chi_d(T) = \frac{Ng^2\mu_B^2}{kT}\frac{2e^{\left(\frac{2J}{kT}\right)} + 10e^{\left(\frac{6J}{kT}\right)} + 28e^{\left(\frac{12J}{kT}\right)}}{1 + 3e^{\left(\frac{2J}{kT}\right)} + 5e^{\left(\frac{6J}{kT}\right)} + 7e^{\left(\frac{12J}{kT}\right)}}.$$

For the fixed g factor equal to 2.00, the results of calculations showed the antiferromagnetic interaction between the chromium atoms, whose magnetic interaction constants were J_{CrCr} = –13.64(4) cm^{-1} for **II** and

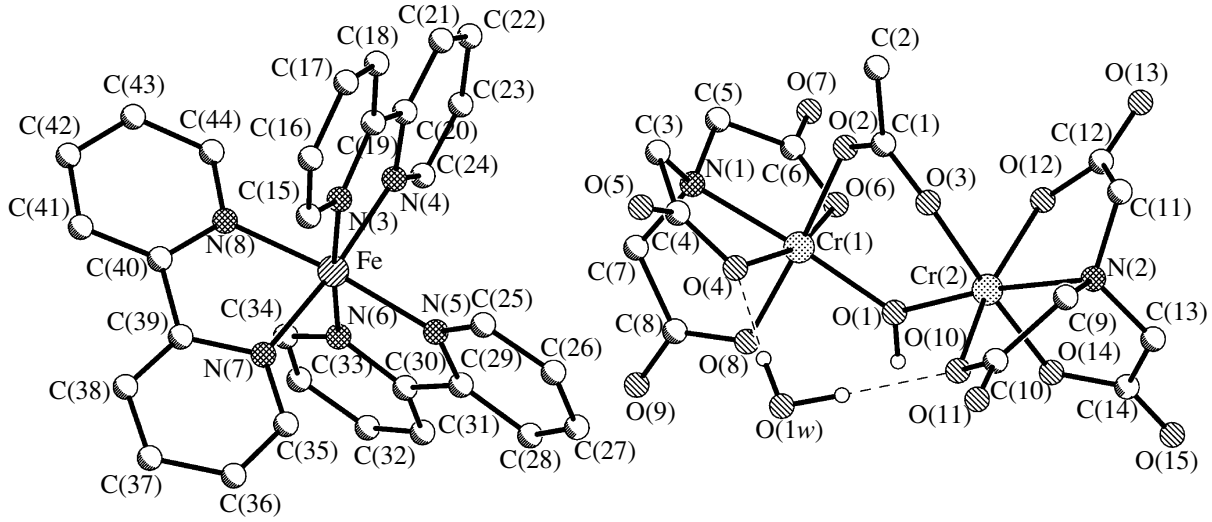


Fig. 1. Structure of the complex $[Fe(Bipy)_3][Cr_2(OH)(Ac)(Nta)_2] \cdot 8H_2O$ (**II**).

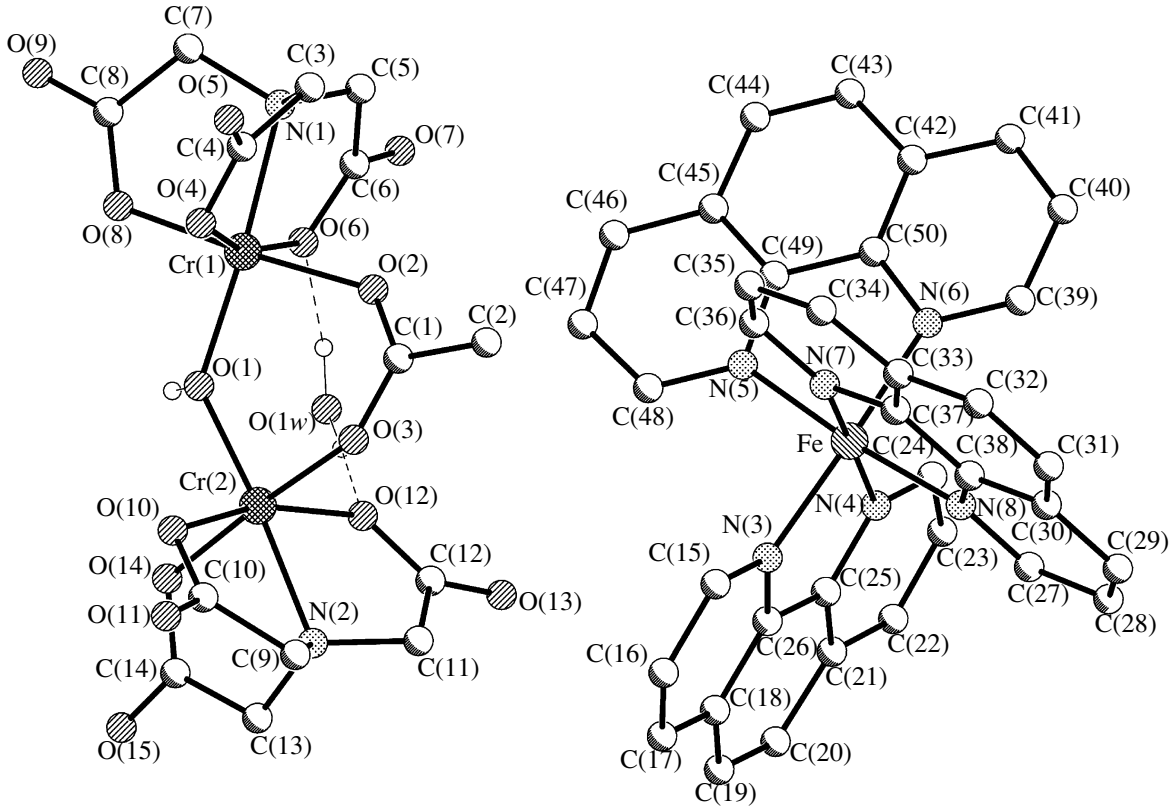


Fig. 2. Structure of the complex $[Fe(Phen)_3][Cr_2(OH)(Ac)(Nta)_2] \cdot 6.25H_2O$ (**III**).

J_{CrCr} = –10.78(5) cm^{-1} for **III**. As the Curie–Weiss parameters, the magnetic interaction constants are close to those in the studied heterometallic chromium compounds with analogous OH^- and Ac^- bridging groups [24, 26, 27]. A slight difference in the J_{CrCr} values for compounds **II** and **III** is the result of violation in coordination of the acetate ion by intermolecular forces of the crystal packing.

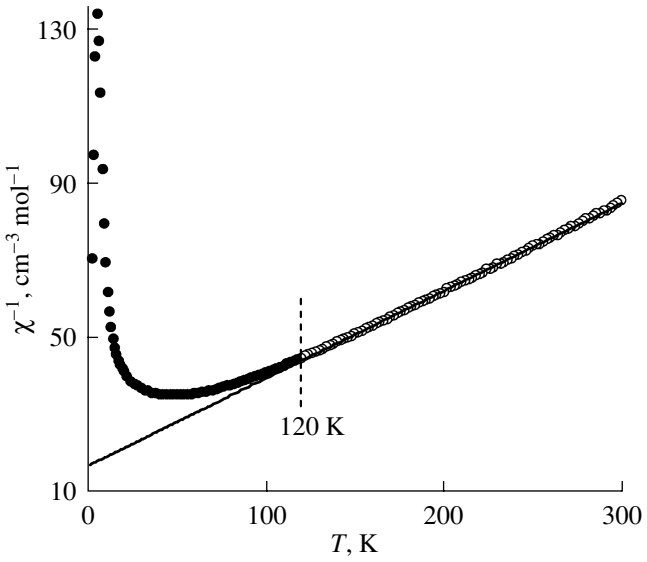


Fig. 3. Temperature dependence of the magnetic susceptibility $[\chi_M(T)]^{-1}$ for compound **II**.

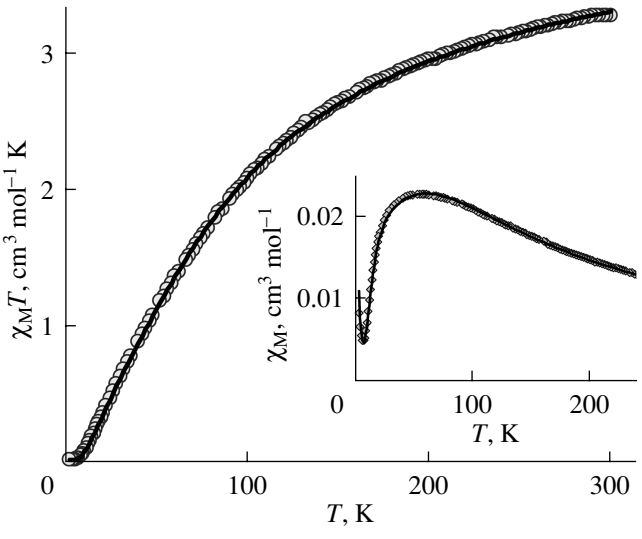


Fig. 4. Temperature dependences of $\chi_M T$ and χ_M for compound **III**. Solid line corresponds to the theoretically determined value according to the model presented in text.

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