MIXED-LIGANDS μ_3-OXO TRINUCLEAR CARBOXYLATES $[Fe_3O(CH_2BrCOO)_{1.5}(CH_2ClCOO)_{4.5}(H_2O)_3]Br_{0.75}Cl_{0.25}$ $5H_2O$ and $[Fe_3O(BrCH_2COO)_6(H_2O)_3]$ $NO_3{\cdot}2.63H_2O$

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Abstract: Two novel μ_3-oxo-centered carboxylate-bridged triiron complexes $[Fe_3O(BrCH_2COO)_6(H_2O)_3]$ $NO_3{\cdot}2.63H_2O$ (**1**) and $[Fe_3O(CH_2BrCOO)_{1.5}(CH_2ClCOO)_{4.5}(H_2O)_3]Br_{0.75}Cl_{0.25}$ $5H_2O$ **(2)** were synthesized and their structures were characterized by X-ray crystallography. The opportunity of mixed-ligand complex formation in iron(III)-bromoacetic acid system was shown. The first co-ordination sphere of the iron atom in compound **2** includes two different carboxylate anions, CH_2BrCOO^- and CH_2ClCOO^- in the capacity of *syn-syn-* bidentate-bridged ligands, while Br^- and Cl^- anions being in the ratio 1:1, formulate the external sphere of the complex. The IR spectra, thermic analysis and magnetic properties of complexes were studied.

Keywords: mixed-ligands complexes; Iron(III) carboxylates; crystal structure, magnetic properties

Introduction

Oxo-centered carboxylate–bridged trinuclear complexes of the type $[M_3(\mu_3\text{-}O)(RCOO)_6L_3]^{n+}$ represent an important class of compounds in transition metal chemistry [1]. The study of trinuclear carboxylates of iron(III) covers a large number of publications. Extensive structural and physicochemical studies of these compounds have been crucial for increasing understanding of bonding and magnetic interactions between proximate metal centers, topics with implications ranging from metalloprotein structures [2-12] to industrial catalysis and molecular materials [13-16]. The relatively large metal-metal distances preclude the possibility of direct metal-metal bonding and the complexes are particularly interesting and are useful models for systematically studying weak metal-metal interactions in multi-nuclear metal complexes.

The oxotrinuclear complexes are known with a wide variety of metal ions, bridging carboxylate anions and monodentate terminal ligands as well as with mixed-valence [17-20] and mixed-metal combinations [21-25]. The clusters which contain various bridge carboxylate ligands in the first coordination sphere are less studied. Among these there can be mentioned compounds with composition $[Fe_3O(RCOO)_n(B)_{6-n}L_3]^{m+}$: where RCOOH are different aminoacids, B= $H_2PO_3^-$, n= 3, m= 4, A= NO_3^- [26]; RCOO= CH_3COO^-, B= $C_2H_5COO^-$, n= 3, m= 1 [27]. Since, the variations in the bridging carboxylates and the monodentate ligands can influence structural and electronic properties of the complexes [28-30], synthesis and study of such complexes remain attractive.

In the present paper we have studied the formation of new complexes in different conditions of iron(III)-bromoacetic acid system which is only described by one structural work in literature [31]. The structure, IR spectra, thermic analysis and magnetic properties of complexes have been investigated.

Results and discussion

The reaction of bromoacetic acid with iron(III) nitrate or chloride in molar ratio 2:1, at sodium alkaline presence, results to the trinuclear compounds with following composition: $[Fe_3O(BrCH_2COO)_6(H_2O)_3]NO_3{\cdot}2.63H_2O$ (**1**) and **[**$Fe_3O(CH_2BrCOO)_{1.5}(CH_2ClCOO)_{4.5}(H_2O)_3]Br_{0.75}Cl_{0.25}{\cdot}5H_2O$ **(2)**. Compound **1** is also formed in the case when iron(III) carbonate was used for neutralization of carboxylic acid. In the reaction containing Cl^- as anion, the formation of the mixed-ligand complex is revealed. The complexes are crystalline solids with red-brown colour. The molecular and crystal structures have been established by single X-ray structural analysis for both complexes. Crystal data, data collection parameters and refinement for **1** and **2** are presented in table 1, while selected bonds lengths and angles – in table 2.

Both **1** and **2** compounds have the similar molecular structure typical for trinuclear iron(III) carboxylates containing a μ_3-O bridge. The iron atoms are described as an almost equilateral triangle and each of them is coordinated by four O atoms of bridging carboxyl groups and the water molecule in the *trans* position to the μ_3-bridging oxygen atom.

The crystal **1** consists of trinuclear complex cations $[Fe_3O(CH_2BrCOO)_6(H_2O)_3]^+$, NO_3^- anions and solvent water molecules in 1:1:2.63 ratio. The outer sphere anions NO_3^- occupy two different systems of special positions on the two-fold axis with the occupancy factor of 0.5. Two solvent water molecules O(6*w*) and O(7*w*) are also located on the two-fold axis with the same occupancy factor. The general position of solvent water molecule O(4*w*) statistically alternates with the position of one of NO_3^- groups in 1:1 ratio. The structure of the complex cation $[Fe_3O(CH_2BrCOO)_6(H_2O)_3]^+$ with the labeling scheme is depicted in figure 1. Three iron atoms define an equilateral

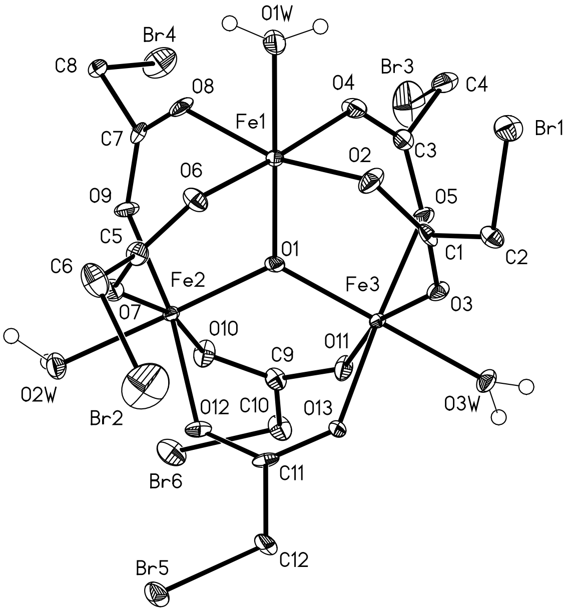


Figure 1. Molecular structure of the complex 1.

triangle with the μ_3-O atom in its centre. The geometrical characteristics of the $[Fe_3O]^{7+}$ core are well compared with those found in $[Fe_3O(CH_2BrCOO)_{1.5}(CH_2ClCOO)_{4.5}(H_2O)_3]^+$ **(2)** and in the other iron carboxylate complexes [18, 31, 32]. The average Fe-Fe distances are equal to 3.307(1) and 3.31(1) Å, while Fe-O(1) adopts the values 1.912(5) and 1.902(3) Å in **1** and **2**, respectively. Six carboxylate groups with *syn-syn* configuration bridge the pairs of Fe(III) atoms in the cluster. The Fe-O_{COO} distances are in the range 2.007(5)-2.039(5)Å for **1** and 1.976(5)-2.043(5)Å for **2.** For both complexes each of the Fe atom exhibits (6O) slightly distorted octahedral environment with very similar geometric characteristics (table 1).

Table 1

Crystallographic data collection and structure determinations for complexes I and II

Compound	**I**	**II**
formula	$C_{12}H_{23}Br_6Fe_3NO_{21.50}$	$C_{12}H_{28}Br_{2.21}Cl_{4.79}Fe_3O_{21}$
formula weight	1172.32	1022.19
crystal system, space group	Orthorhombic, $C222_1$	Monoclinic, $P2_1/n$
a, Å	18.778(4)	12.580(3)
b, Å	19.061(4)	14.554(3)
c, Å	18.393(4)	17.947(4)
α, deg	90.0	90.0
β, deg	90.0	96.13(3)
γ, deg	90.0	90.0
V, Å^3	6583(2)	3267.1(13)
Z, ρ_{calcd}, g cm^{-3}	8, 2.366	4, 2.018
λ, Å	0.71073	0.71073
T, K	120	150

$\mu(MoK_{\alpha})$,cm^{-1}	8.669	4.485
GOOF for F^2	1.067	1.042
^{a}R $[I>2\sigma(I)]$	0.0440	0.0570
^{b}wR (all data)	0.0532	0.0717
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, eÅ^3	1.576 and -1.209	1.458 and -0.888

$^{a}R = \sum||F_o| - |F_c||/\sum|F_o|$. $^{b}wR = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$

Table 2

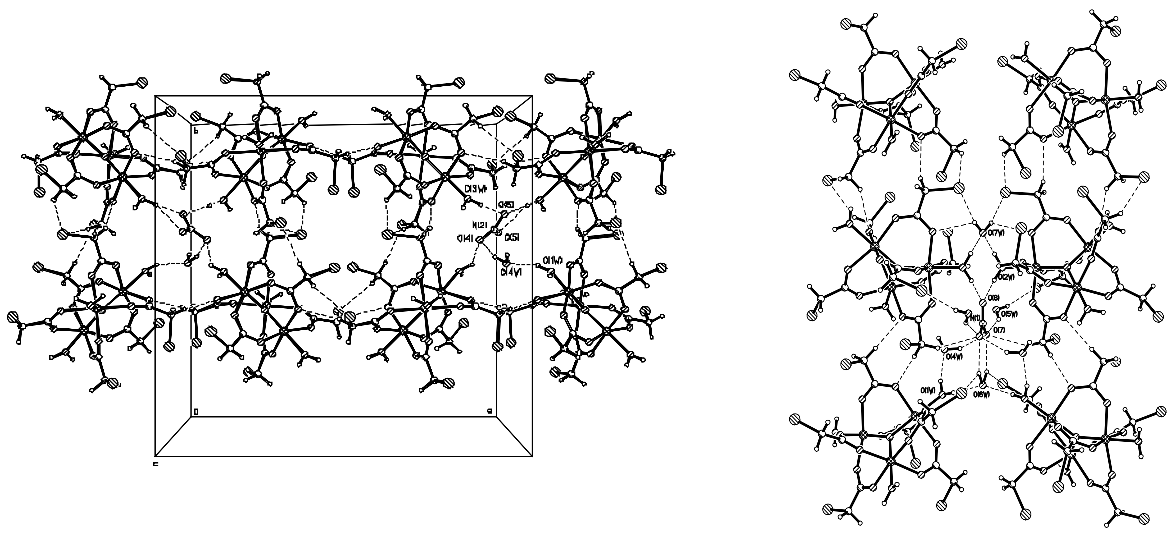
Selected bond lengths (Å) and angles (°) in structures 1 and 2.

Bond	Compound 1	Compound 2
Fe1-O1	1.912(5)	1.902(3)
Fe1-O2	2.005(5)	2.005(4)
Fe1-O8	2.008(5)	1.980(4)
Fe1-O6	2.022(5)	2.037(4)
Fe1-O4	2.023(5)	2.023(4)
Fe1-O1w	2.051(5)	2.073(4)
Fe2-O1	1.904(5)	1.913(3)
Fe2-O10	2.008(5)	2.048(4)
Fe2-O7	2.009(5)	2.014(4)
Fe2-O9	2.011(5)	2.039(4)
Fe2-O12	2.023(5)	2.012(4)
Fe2-O2w	2.094(5)	2.030(4)
Fe3-O1	1.915(5)	1.919(3)
Fe3-O11	2.016(5)	2.005(4)
Fe3-O3	2.020(5)	2.018(4)
Fe3-O13	2.028(5)	1.998(4)
Fe3-O3w	2.031(5)	2.031(4)
Fe3-O5	2.037(5)	2.044(4)

Angle	1	2
O1-Fe1-O2	97.7(2)	96.96(15)
O1-Fe1-O8	95.9(2)	94.56(16)
O2-Fe1-O(8	166.1(2)	168.47(16)
O(1-Fe1-O6	92.6(2)	95.99(15)
O2-Fe1-O6	89.1(2)	84.32(17)
O8-Fe1-O6	92.6(2)	93.97(17)
O1-Fe1-O4	91.5(2)	93.28(15)
O2-Fe1-O4	90.3(2)	91.99(17)
O8-Fe1-O4	87.0(2)	87.87(17)
O6-Fe1-O4	175.8(2)	170.38(16)
O1-Fe1-O1w	178.0(2)	177.92(16)
O2-Fe1-O1w	83.7(2)	84.40(16)
O8-Fe1-O1w	82.6(2)	84.10(17)
O6-Fe1-O1w	88.7(2)	85.71(15)
O4-Fe1-O1w	87.1(2)	85.08(16)
O1-Fe2-O10	98.9(2)	97.07(15)
O1-Fe2-O7	94.8(2)	94.35(15)
O10-Fe2-O7	166.1(2)	168.48(15)
O1-Fe2-O9	95.1(2)	94.66(15)
O10-Fe2-O9	86.9(2)	85.83(16)
O7-Fe2-O9	94.0(2)	91.73(17)
O1-Fe2-O12	95.1(2)	93.43(15)
O10-Fe2-O12	89.2(2)	89.60(16)
O7-Fe2-O12	87.5(2)	91.25(17)

O9-Fe2-O12	169.5(2)	171.14(16)
O1-Fe2-O2w	179.0(2)	178.48(16)
O10-Fe2-O2w	81.3(2)	83.84(15)
O7-Fe2-O2w	85.0(2)	84.77(16)
O9-Fe2-O2w	83.9(2)	86.62(16)
O12-Fe2-O2w	85.9(2)	85.35(15)
O1-Fe3-O11	97.9(2)	96.13(15)
O1-Fe3-O3	96.6(2)	97.56(15)
O11-Fe3-O3	165.4(2)	166.27(16)
O1-Fe3-O13	92.0(2)	93.97(15)
O11-Fe3-O13	88.6(2)	88.11(17)
O3-Fe3-O13	89.3(2)	92.01(16)
O1-Fe3-O3w	179.5(2)	176.52(15)
O11-Fe3-O3w	81.6(2)	80.63(15)
O3-Fe3-O3w	83.8(2)	85.66(15)
O13-Fe3-O3w	88.0(2)	87.20(16)
O1-Fe3-O5	91.4(2)	93.05(15)
O11-Fe3-O5	89.5(2)	86.91(17)
O3-Fe3-O5	91.8(2)	91.29(16
O13-Fe3-O5	176.3(2)	171.79(16)
O3W-Fe3-O5	88.6(2)	85.55(16)

In the crystal structure of **1** all components interact via a system of O-H…O, C-H…O, O-H…Br and C-H…Br hydrogen bonds that lead to the formation of 3D supramolecular aggregate. The structural functions of two nitrate anions are different. One of them is located in the closed cages, which are formed by the packing of trinuclear cations in the crystal (figure 2a). Thus, it is connected directly or through O(4*w*) by hydrogen bonds with the co-ordinated water molecules of four next complexes. It results in the layers running perpendicular to the *c* axis in the unit cell and being additionally stabilized by the intermolecular C-H…Br contacts. The second NO_3^- group is located in the space between these layers and consolidate bromine atoms, co-ordinated O(1*w*), O(2*w*) and solvated O(5*w*), O(6*w*), O(7*w*) water molecules (figure 2b). O(7*w*) water molecule realises its donor functions in the links with O(2*w*) and bromine atoms, thus provides the interaction between four μ_3-oxo clusters in the crystal.



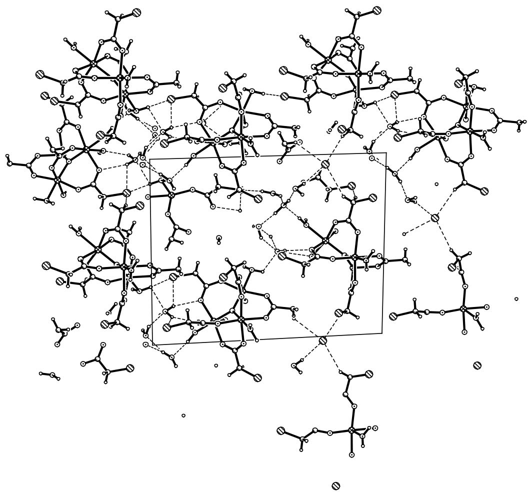
a) b)

Figure 2. *a* and *b*. Structural function of two NO_3^- anions in crystal **1**.

The final chemical composition and structure of compound **2** was only proved by X-ray analysis. The first co-ordination sphere of iron includes two different carboxylate anions, CH_2BrCOO^- and CH_2ClCOO^- in the capacity of *syn-syn-* bidentate ligands being in 1:3 ratio, while Cl^- and Br^- anions are counter-ions.

The presence of the bromide anion as counter-ion can be only explained by the suggestion that in the reactive medium in the conditions of high concentration of chlorine ions the partial replacement of bromine atoms in bromoacetic acid molecule by chlorine takes place. Iron(III) chloride and monobromoacetic acid were used as the initial substances for the complex preparation. Thus, the final complex composition for **2** corresponds to the formula $[Fe_3O(CH_2BrCOO)_{1.5}(CH_2ClCOO)_{4.5}(H_2O)_3]Br_{0.75}Cl_{0.25}\cdot 5H_2O$.

The packing of the complexes **2** in the crystal affords the closed cavities, which are filled by the water tetramer associates, $[H_2O]_4$, as showed in figure 3. They are bound with the nearest trinuclear complexes by the hydrogen bonds through bromine (or chlorine) atoms of acid residue, and co-ordinated water molecules. Each $[H_2O]_4$ tetramer is built



are exothermic ones and correspond to the loss of mass till 69 %. The fifth, terminal process occurs at 330-420 ^{o}C and apparently corresponds to the iron(III) oxide formation (the residue is 22 – 21 %).

The thermic decomposition of the second compound differs essentially from the first one. The process mainly occurs in the range of the temperatures of 40 – 180^{o}C with the maximum at 100 ^{o}C. Apparently, this temperature interval ensures the removal of the ligands with the formation of iron oxyhalogenides. This endothermic process corresponds to the mass loss of ~ 34 %. In the range 180 - 340 ^{o}C the further mass loss of 7 % takes place. Unexpectedly on the TGA curve the endothermic peak appears in the range 400 – 420 – 440 ^{o}C, which does not correspond to the mass change. We suggest the possibility of phase transition of the decomposition products in this temperature interval. In the range of 560 – 730 ^{o}C the further loss of the substance equal 5–6% is observed that may correspond to the removal of the definite part of iron halogenides. Even at 800 ^{o}C the stabilization of the decomposition process does not occur.

The iron(III) oxide should be considered as a final product of the thermic decomposition of compounds **1** and **2**. The first two decomposition steps for the studied iron(III) carboxylates correspond to the removal of water molecules and carboxylate ions with the formation of the product characterized by the tetrahedral environment of the central metal *via* anions (O^{2-}), (Cl^{-1}), (Br^{-1}). Apparently each cluster keeps its framework {Fe_3O}, where chloride and bromide anions complete the coordination number of each iron cation till four. Further increase of the temperature results in the removal of iron chloride and/or bromide with the simultaneous formation of iron(III) oxide. The additional study could help to clarify the mechanism of decomposition of these compounds.

IR spectra of the synthesized substances exhibit all the main characteristic frequencies typical for the carboxylate anions, C-Hal bonds and water. The assignment of the absorption bands was carried out according with [33]. In the range of 3650 – 3000 cm^{-1} the wide band ν(OH) is characteristic for the H-bonded water molecules. On the background of this wide band two peaks of the medium intensity are exhibited at 3570 and 3540 cm^{-1}, which can be attributed to the non-coordinated water molecules. The appearance of a band at 920 cm^{-1} is natural and corresponds to the deformation vibrations of OH moiety, δ(HOH). Coordinated carboxyl groups exhibit the frequencies at 1600 и 1415 cm^{-1} for (1) and at 1608 и 1426 cm^{-1} for (2) which correspond to the bridge COO^- moieties (Δν = 172 – 185 cm^{-1}). The single band of the medium intensity at 1220 cm^{-1} for (**1**) and two splitting absorption bands at 1260-1256; 1232-1220 cm^{-1} for **2**, can be attributed to the combination of the vibrations δ(OH) + δ(C-O) of two these moieties, O-H and (C-O) [33].

Complex **2** is characterized by the band at 794 cm^{-1} of the medium intensity, which is absent in the IR spectrum of **1**, and it can be attributed to the stretching vibrations ν(C-Cl). The stretching vibrations ν(C-Br) at ~570 см$^{-1}$ are characteristic for the both complexes. The very weak band at 850 cm^{-1} in the IR spectrum of **1** corresponds to the $\nu_2(NO_3^-)$ frequency of nitrate anion. The band at 680 ± 5cm $^{-1}$ is present in the spectra of both **1** and **2** and it is assigned to the bending vibrations of δ(OCO), while the band at 725 ± 5 cm^{-1} is assigned to the - ρ (COO) [1, 33]. In the 960 - 850 cm^{-1} range of the spectrum there are three bands: 950, 928 cm^{-1} for **2** and 950 cm^{-1} for **1** assigned to ν(C-C) and δ (O-H) at 885 ± 5 cm^{-1}. Asymmetric vibrations of the {Fe_3O} core are identified at about 600 – 605 cm^{-1} ($\nu_{as}(Fe_3O)$). Thus, the positions of the absorption bands ν(COO) and $\nu_{as}(Fe_3O)$ in the IR spectra of iron carboxylates confirm the coordination mode of the acid residues to the central metal atom in according with X-ray data.

Magnetic measurements for the complex **1** were made at the range 300 K - 2 K and the results are shown in the figure 5. The magnetic moments of complexes **1** and **2** per one iron atom were found to be 3.28 and 3.17 B.M. (RT) respectively, that is essentially lower than the pure spin value for iron(III) (μ_{ef}= 5.92 B.M.). These observations

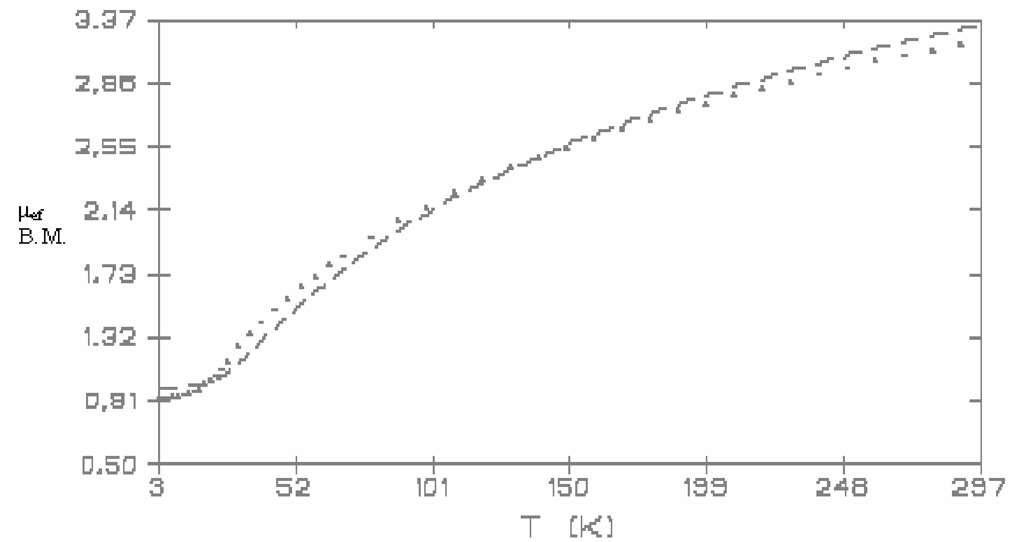


Figure 5. The temperature dependence of the experimental and theoretical values of $\mu_{ef.}$ for complex **1**.

indicate the antiferromagnetic interaction between the paramagnetic metal ions. The temperature dependence of magnetic properties of **(1)** was described by Heisenberg-Dirac-van Vleck (HDVV) approximation $\mathbf{H = -2J\,\Sigma\,(S_i\,S_j)}$ [34, 35] for complex with D_{3h} symmetry. The best fit between experimental and theoretical data have been obtained by the value of (–J) equal to ~40 cm^{-1}, which is in good concordance with the respective parameter for other trinuclear oxobridged iron(III) carboxylates [32, 36].

Experimental

General: The following compounds $Fe(NO_3)_3{\cdot}9H_2O$, monobromacetic acid, sodium hydroxide were obtained from commercial sources and used as received. The carbon and hydrogen content was determined by standard micro-methods in the microanalytical group of the Institute of Chemistry of the Academy of Sciences of Moldova. IR spectra of polycrystalline samples were recorded (4000-400cm^{-1}) as oil mulls on a Specord M-75 spectrophotometer. TG studies were performed on a Paulik-Paulik-Erdey derivatograph in air, with platinum crucible, Al_2O_3 as calibration standard and at a speed of heating equal to 5 ^oC/min. DTG - 1/5; DTA - 1/10; TG - 100/100. T_{max} =1000 ^oC. Variable temperature susceptibility was measured with an Oxford Instruments Vibrating Sample Magnetometer (VSM) working between 0 and 12 T and in the 1.5–350.0K temperature range.The diamagnetic Pascal's constants were used to correct the magnetic values [35]. To determine the value of μ_{eff} the relation $(\mu_{eff})_M = \sqrt{8\chi_M T}$ (B.M.) was used. The J parameter was calculated by least squares fitting using the experimental data fitting Program "Minsk".

Synthesis. **$[Fe_3O(CH_2BrCOO)_6(H_2O)_3]NO_3{\cdot}2.63H_2O$ (1)**

(**a**) A solution of $BrCH_2COOH$ (1.39 g, 10 mmol) in distilled water (10 cm^3) was neutralized with solid NaOH (0.4 g, 10 mmol). To this solution was added (dropwise) $Fe(NO_3)_3{\cdot}9H_2O$ (2.02 g, 5 mmol) in distilled water (20 cm^3) while stirring, forming a deep red solution. The resulting solution was heated up on a water bath at temperature 50^{o}C for 30 minutes and than cooled to room temperature. After two days the crystalline dark red precipitate was collected by filtration, washed with ethanol, and dried in air at room temperature. Yield: 1.5 g (77%). Found, %: C 12,03, H 1.90, N 1.14, Fe 14.00. Calc. for $C_{12}H_{23.}Br_6Fe_3NO_{21..50}$ (1172.32), %: C 12.28, H 1.98, N 1.19, Fe 14.29.

(***b***) The complex **1** was also obtained using iron carbonate by the following method. To the warm solution of $BrCH_2COOH$ (1.39 g, 10 mmol) in distilled water (20 cm^3) the corresponding amount of iron carbonate was added while stirring. The equivalence point was determined proceed from the effervescence of CO_2. Step-by-step the color was changing to deep red. After the termination of the CO_2 effervescence the heating on the water bath was continued for 15-20 minutes. The resulting solution was filtrated off and the aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ (0.67 g, 1.6 mmol) was added. After two days the crystalline dark red precipitate was collected by filtration, washed with ethanol, and air dried at room temperature. Yield: 1.4 g (72%). Found, %: C 12.03, H 2.1, N 1.17, Fe 14.05. Calc. for $C_{12}H_{23}Br_6Fe_3NO_{21..50}$ (1172.32), %: C 12.28, H 1.98, N 1.19, Fe 14.29.

$[Fe_3O(CH_2BrCOO)_{1.5}(CH_2ClCOO)_{4.5}(H_2O)_3]Br_{0.75}Cl_{0.25}$ $5H_2O$ (2). A solution of $BrCH_2COOH$ (1.39 g, 10 mmol) in distilled water (10 cm^3) was neutralized with solid NaOH (0.4 g, 10 mmol). To this solution was added (dropwise) $FeCl_3{\cdot}6H_2O$ (1.35 g, 5 mmol) in distilled water (20 cm^3) while stirring, forming a deep red solution. The resulting solution was heated up on a water bath at temperature 50^{o}C for 30 minutes and than cooled to room temperature. After several days the microcrystalline dark red precipitate was collected by filtration, washed with ethanol, and air-dried at room temperature. Yield: 1.1 g (67%). Found, %: C 13.89, H 2.70, Fe 16.07. Calc. for $C_{12}H_{28}Br_{2.21}Cl_{4.79}Fe_3O_{21}$ (1022.19), %: C 14.08, H 2.73, Fe 16.38.

X-ray crystallography: All crystallographic measurements were carried out with a KM4CCD diffractometer equipped with a graphite monochromated Mo-K_α radiation source. For both **1** and **2** crystals 532 frames were measured in four series, rotated by φ=0.75° from each other and a detector-to-crystal distance has been equal to 60 mm. All data processing was performed with the use of the Kuma Diffraction program package (Wroclaw, Poland). Intensity data were corrected for the Lorentz and polarization effects. The structure was solved by direct methods using SHELXS-86 [37] and refined by full-matrix least-squares on F^2 using SHELXL-93 [38]. All measured reflections were included in the refinement process. The non-H atoms were refined with anisotropic displacement parameters. The positions of H-atoms bonded to C atoms were fixed in the idealized positions and allowed to ride. Positional parameters of the water H-atoms were obtained from the difference Fourier syntheses and verified by the geometric parameters of hydrogen bond and are summarized in Table1, while bond lengths and angles - in Table 2.

Crystallographic data for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplimentary publication. CCDC reference numbers 701028 and 701029. Copies of data can be obtained on application by <deposit@ccdc.cam.ac.uk>. Main crystallographic parameters and structure refinement details are summarized in table 1, while selected bond lengths and angles in table 2.

Conclusions

Two novel μ_3-oxo-centered carboxylate-bridged triiron complexes $[Fe_3O(BrCH_2COO)_6(H_2O)_3]NO_3 \cdot 2.63H_2O$ (**1**) and $[Fe_3O(CH_2BrCOO)_{1.5}(CH_2ClCOO)_{4.5}(H_2O)_3]Br_{0.75}Cl_{0.25}$ $5H_2O$ (**2**) have been synthesized and their structures were refined by single X-ray diffraction. The opportunity of mixed-ligand complex formation in iron(III)-bromoacetic acid system was shown. In the reaction medium containing iron(III) chloride as initial, the partial replacement of bromine atoms in bromoacetic acid molecule by chlorine takes place. The first co-ordination sphere of the iron atom in compound **2** includes two different carboxylate anions, CH_2BrCOO^- and CH_2ClCOO^- in the capacity of *syn-syn*-bidentate-bridged ligands, while Br^- and Cl^- anions being in the ratio 1:1, formulate the external sphere of the complex. The magnetic moments of the complexes **1**, **2** per one iron atom founded 3.28 and 3.17 B.M.(RT) respectively, indicate the antiferromagnetic interaction between the paramagnetic metal ions with the value of $-J = 40.2$ cm^{-1} calculated for the complex **1.**

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