Polynuclear iron(III) pivalates

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The formation of magnetically active polynuclear Fe^{III} pivalates in the $FeSO_4 \cdot 7H_2O$—$KOOCCMe_3$ system was studied. The reaction of $FeSO_4 \cdot 7H_2O$ (**1**) with $KOOCCMe_3$ in EtOH in air afforded the antiferromagnetic trinuclear complex $[Fe_3O(OOCCMe_3)_6(H_2O)_3]^+[OOCCMe_3]^- \cdot 3EtOH$. A change of the solvent (EtOH) in this system to a 40 : 1 benzene—THF mixture resulted in the formation of the antiferromagnetic hexanuclear cluster $[Fe_6(O)_2(OH)_2(OOCCMe_3)_{12}(HOOCCMe_3)(THF)] \cdot 1.5C_6H_6$. The addition of trimethylacetic acid to EtOH and recrystallization from hexane gave rise to the antiferromagnetic coordination polymer $[K_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(H_2O)_2]_n$ (**7**). Recrystallization of the latter from acetonitrile afforded the antiferromagnetic tetranuclear complex $K_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(MeCN)_2$. The structures of these compounds were established by X-ray diffraction analysis, and their magnetic susceptibilities and thermal decomposition were investigated.

Key words: polynuclear iron complexes, carboxylate ligands, synthesis, X-ray diffraction analysis, magnetic properties.

Generally, polynuclear trimethylacetate complexes with iron atoms are readily soluble in usual organic solvents and are of interest in many respects. For example, complexes with three or six Fe^{III} atoms hold promise as components of the homogeneous catalytic Gif system used for oxidation of hydrocarbons.[1] High solubility of polynuclear complexes in hydrocarbon solvents allows one to readily transfer iron ions to nonaqueous media, which is of importance for the preparation of iron-containing films on the surface of various materials. In addition, mass-spectrometric studies demonstrated that carboxylate ligands can be eliminated from such iron complexes with the resulting increase in the nuclearity of the metal core to give finally oxide systems.[2—4] Polynuclear iron carboxylates possess unusual magnetic properties, because the Fe^{III} or Fe^{II} atoms in these complexes exist in the high-spin state and exhibit spin-spin exchange interactions.[5—16] An intramolecular electron transfer between the metal centers was observed[17] in the heterospin $Fe_3O(OOCCMe_3)_6L_3$ compounds (L = Py or $HOOCCMe_3$). Polynuclear iron pivalates are generally prepared from either iron salts or highly dispersed metal. Depending on the nature of the starting metal-containing reagent, either homo-[1—3,8,18] or heterospin[16,17] polynuclear complexes of different nuclearity and, as a rule, containing Fe_3O fragments are produced.

Recently, we have found[19] that the $FeSO_4 \cdot 7H_2O$ complex (**1**) can serve as a convenient iron-containing reagent for the synthesis of pivalates. The reaction of this reagent with potassium trimethylacetate in the presence of Me_3CCOOH in inert atmosphere affords the antiferromagnetic $[Fe_3(\mu_3\text{-}OH)(\mu_2\text{-}OOCCMe_3)_6(HOOCCMe_3)_3]^-$ anion (**2**) containing a triangular metal core consisting of Fe^{II} atoms. This anion is highly sensitive to oxygen. The reaction of compound **2** with 2,3-lutidine produces the dinuclear antiferromagnetic complex with divalent iron, $(2,3\text{-}Me_2C_5H_3N)_2Fe_2(\mu\text{-}OOCCMe_3)_4$ (**3**), having a Chinese-lantern structure.[14]

In the present study, we examined the formation of polynuclear iron(III) pivalates in the $FeSO_4$—$KOOCCMe_3$ system in the presence of atmospheric oxygen and investigated thermal decomposition of the new iron trimethylacetate complexes.

Results and Discussion

Tri- and hexanuclear iron(III) trimethylacetates

Earlier,[14,19] it has been found that the reaction of $FeSO_4 \cdot 7H_2O$ (**1**) with potassium trimethylacetate in inert atmosphere affords iron(II) trimethylacetate complexes. Our experiments demonstrated that the hetero-

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geneous reaction of salt **1** with an excess of $KOOCCMe_3$ in EtOH (50 °C, the reagent ratio was 1 : 3) in air was accompanied by oxidation of Fe^{II} to form the $[Fe_3O(OOCCMe_3)_6(H_2O)_3]^+[OOCCMe_3]^- \cdot 3EtOH$ compound (**3**). An analog of compound **3**, *viz.*, the $[Fe_3O(OOCCMe_3)_6(H_2O)_3]^+[OOCCMe_3]^- \cdot 2HOOCCMe_3$ complex (**4**), has been synthesized earlier[3] from iron(III) nitrate and an excess of trimethylacetic acid. Presumably, complex **3** is generated from the structurally similar trinuclear precursor, *viz.*, a Fe^{II} compound similar to complex **2**, which we have isolated earlier. The formation of compound **3** was also observed in the reaction of $FeCl_3 \cdot 6H_2O$ with potassium trimethylacetate in ethanol in air. The crystals of compound **3** contain three ethanol solvate molecules, which are not coordinated to the metal atoms, as opposed to the known analog **4** containing two solvate molecules and another known $[Fe_3O(OOCCMe_3)_6(MeOH)_3]^+$ cation,[2] in which the solvate molecules are bound to the metal atoms.

Compound **3** was studied by X-ray diffraction analysis. In the cation of molecule **3** possessing the crystallographic C_2 symmetry, three iron atoms located at nonbonded distances (Fe...Fe, 3.292(1) Å) are linked to each other *via* the tridentate-bridging oxo oxygen atom to form an equilateral triangle (Fe—O, 1.9008(11) Å). The iron atoms are additionally linked to each other *via* three pairs of the bridging trimethylacetate ligands (Fe—O, 2.007(2) Å) (Fig. 1). The octahedral environment of each Fe^{III} atom involves although the oxygen atoms of the water molecules (Fe—O, 2.065(3) Å).

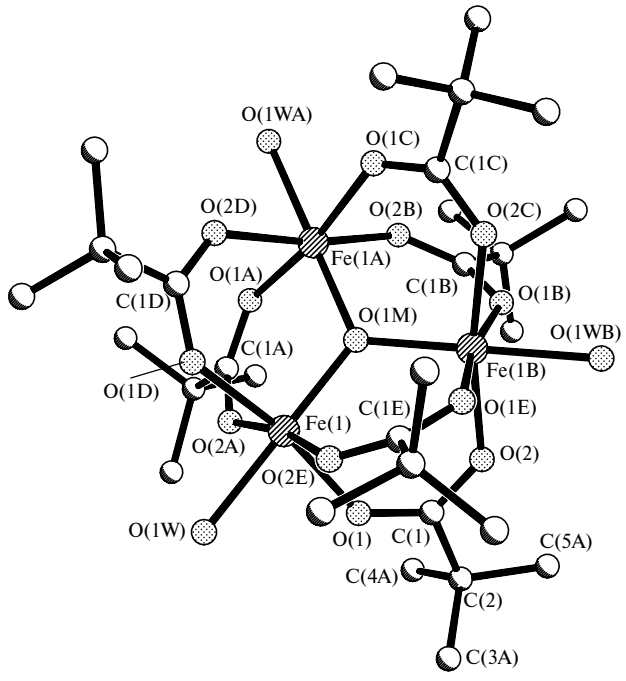

Fig. 1. Structure of the $[Fe_3O(OOCCMe_3)_6(H_2O)_3]^+$ cation in complex **3**.

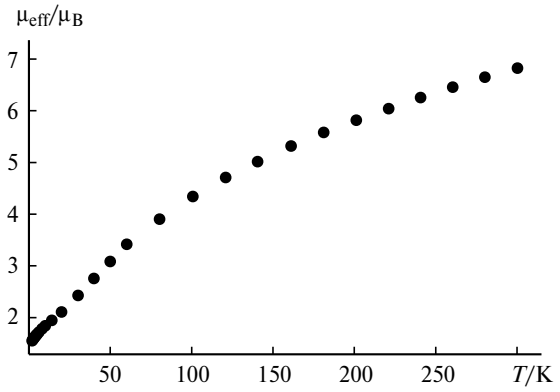

Fig. 2. Temperature dependence of the effective magnetic moment for complex **3**.

Like other trinuclear iron(III) carboxylate oxo clusters,[2,5–12] complex **3** exhibits antiferromagnetic properties. Its effective magnetic moment decreases monotonically from 6.83 to 1.55 μ_B (per overall molecule) in a 300—2 K temperature range (Fig. 2). Interestingly, the lowest value of the effective magnetic moment for compound **3** (1.4 μ_B (2 K)) is substantially smaller than the calculated value (1.73 μ_B) on the assumption of complete spin coupling through antiferromagnetic exchange interactions. Apparently, this effect is determined by additional antiferromagnetic intermolecular interactions, resulting in a further decrease in the magnetic moment.

A change of the solvent in this reaction to a 40 : 1 benzene—THF mixture has a substantial effect on the character of the final product. In this medium, the reaction of iron sulfate with potassium pivalate (in a ratio of 1 : 3) at 80 °C was accompanied by gradual dissolution of the starting sulfate to give a brown solution, from which the hexanuclear trimethylacetate cluster was isolated as a solvate with benzene, $[Fe_6(O)_2(OH)_2(OOCCMe_3)_{12}(HOOCCMe_3)(THF)] \cdot 1.5C_6H_6$ (**5**).

X-ray diffraction analysis demonstrated that the metal core of the complex consists of two triangular Fe_3O fragments (Fe...Fe are 3.423(4), 3.291(4), and 3.260(4) Å in one triangle and 3.258(4), 3.439(4), and 3.264(4) Å in another triangle; Fe—O are 1.962(5), 1.940(5), and 1.855(5) Å in one triangle and 1.930(6), 1.950(5), and 1.867(5) Å in another triangle), which are linked to each other *via* two bridging hydroxo groups (Fe—O, 1.963(6), 1.940(5), 1.990(6), and 1.963(5) Å) and two bridging trimethylacetate ligands (Fe—O, 1.998(6) Å) (Fig. 3). In addition, the iron atoms in the triangles are linked *via* five bridging trimethylacetate ligands (Fe—O, 2.012(7) Å). The triangular fragments differ in the environment of the peripheral iron atoms. One of these triangles contains the metal atom terminally coordinated by the Me_3CCOOH molecule (Fe—O, 2.172(6) Å). In another triangle, the

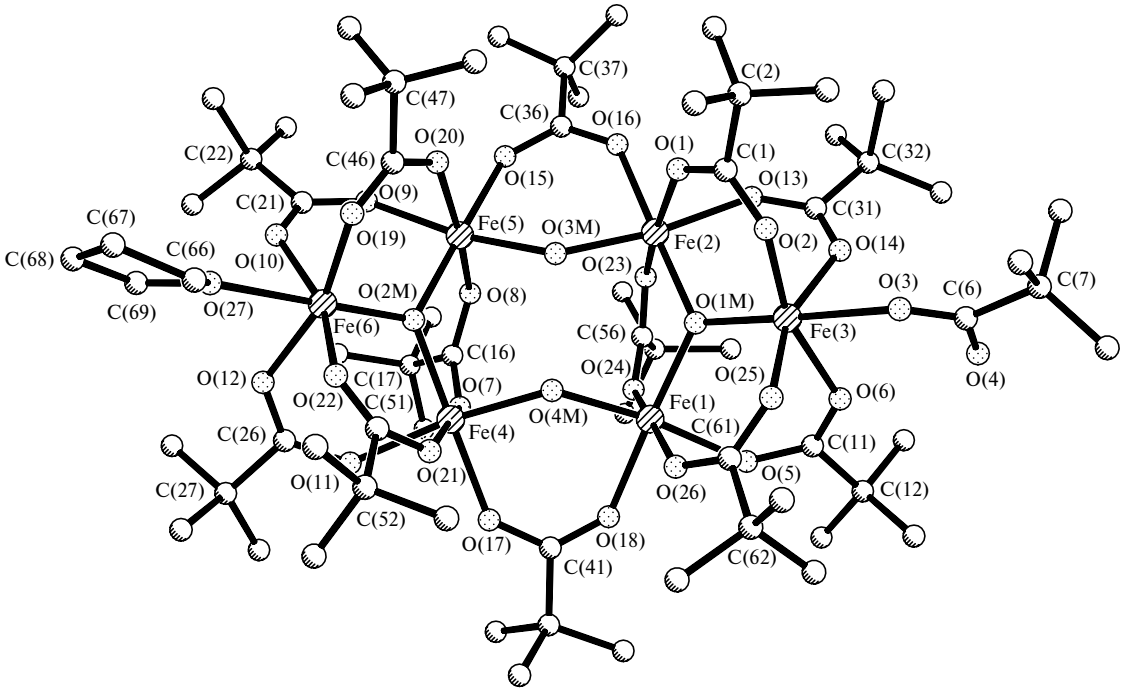

Fig. 3. Structure of hexanuclear complex **5** (benzene solvate molecules are omitted).

iron atom is coordinated by the THF molecule (Fe—O, 2.200(8) Å).

Compound **5** exhibits antiferromagnetic properties. Its effective magnetic moment (calculated per overall molecule) decreases from 7.63 to 1.19 μ_B in a 300—2 K temperature range (Fig. 4).

The formation of hexanuclear pivalate $Fe_6(O)_2(OH)_2(OOCCMe_3)_{12}$ (**6**) has been observed earlier upon thermolysis of complex **4** in tetradecane[3] at temperatures above 200 °C. However, complex **6** contains no terminal ligands bound to the peripheral iron atoms, and the latter have a coordination number of 5. Apparently, a cluster analogous to complex **5** is intermediate in the series **4**→**6** and is formed under milder conditions.

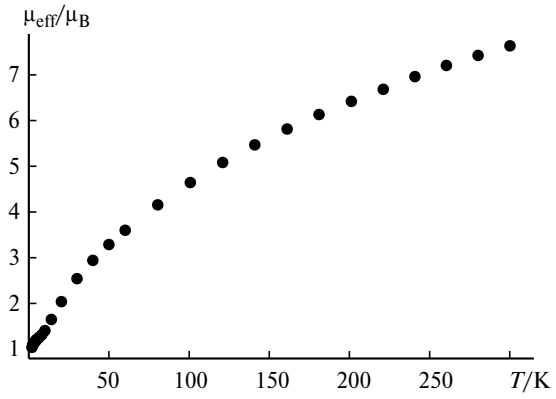

Fig. 4. Magnetic properties of complex **5**.

Study of solid-state thermolysis of trinuclear complex **3** demonstrated that this compound is stable up to 56 °C. In a temperature range of 60—100 °C (Fig. 5), the ethanol solvate molecules were eliminated (weight loss was 12.6±0.5%, the calculated fraction of ethanol in complex **3** is 12.74%). In the temperature range of 100—140 °C, the weight loss was 4.0±0.5% (three moles of H_2O account for 4.99%). Apparently, only two molecules of H_2O were removed in this temperature range, which is confirmed by the value of the second thermal effect. The processes occurring in a range of 60—140 °C were accompanied by energy absorption (endotherm resulting from a superposition of two effects) (see Fig. 5).

A separate integration of the superimposed thermal effects was performed. The first thermal effect is 120±8 kJ mol^{-1}, which is comparable with the heat of evaporation of three ethanol molecules. The second thermal effect is 86±8 kJ mol^{-1}, which is comparable with the thermal effect of evaporation of two water molecules. At temperatures above 140 °C, further stepwise thermal decomposition occurred. The first step of this process (160—190 °C) was also endothermic; the weight loss was 10.1±1.0%. This corresponds to removal of one trimethylacetic acid molecule (one mole of Me_3CCOOH in complex **3** accounts for 9.42%) generated upon the rearrangement of the complex (apparently form the Me_3CCOO^- anion and the proton of the water molecule). The last step (300—345 °C) was also endothermic, but the thermal effect was more pronounced. At temperatures above 350 °C, the sample weight remained unchanged, but a

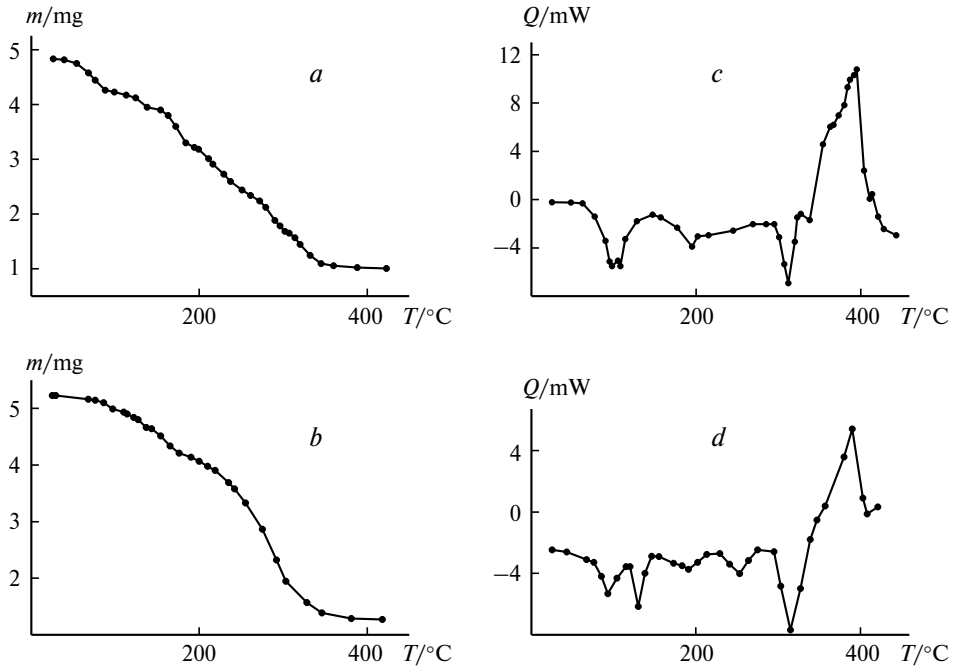

Fig. 5. Characteristics of thermolysis of complexes **3** and **5**: the integral dependence of the change in the weight on the temperature for complexes **3** (*a*) and **5** (*b*); the temperature dependence of the heat flow for complexes **3** (*c*) and **5** (*d*).

large amount of energy was released due, apparently, to the formation of the crystal structure of the decomposition product. The total weight loss throughout the range of investigation was 77.4±1.0%, and the weight of the solid residue was 22.6%. Powder X-ray diffraction study demonstrated that decomposition gave rise to α-Fe_2O_3 (Table 1). The theoretical percentage of Fe_2O_3 in the starting compound was 22.1%. Taking into account the accuracy of experimental investigations (determination of the weight loss and the accuracy of powder X-ray diffraction data), it can be stated that the probability of the presence of other components (such as free metal, oxide of metal in another oxidation state, or carbide) in the decomposition product is at most 4 wt.%.

Thermal decomposition of hexanuclear complex **5** also proceeded stepwise. In a temperature range of 70—145 °C, there are two regions of weight loss, each being accompanied by an endotherm (see Fig. 5). The weight loss in this temperature range is 12.0±1.0%. The percentage of solvate benzene in molecule **5** is 11.58%, *i.e.*, stepwise elimination of solvate benzene occurs. In a temperature range of 150—190 °C, a pronounced step of weight loss (7.9±1.0%) accompanied by an endotherm is observed (see Fig. 5). Apparently, this step corresponds to elimination of the coordinated molecules of tetrahydrofuran and trimethylacetic acid (percentages of THF and Me_3CCOOH in molecule **5** are 3.56 and 5.04%, respectively). The total weight loss throughout the range of investigation was 73.4±1.0%, and the weight of the solid residue was 26.6%. Powder X-ray diffraction study demonstrated that decomposition afforded metastable γ-Fe_2O_3 (Table 2). The calculated percentage of Fe_2O_3 in molecule **5** is 26.4%. As in the case of compound **3**, the probability of the presence of other components in the decomposition product is at most 4 wt.%. Interestingly, the character of the thermal effects for complex **3** at temperatures above 190 °C is qualitatively identical to that for complex **5** (Fig. 6). This

Table 1. Powder X-ray diffraction analysis of the decomposition product of compound **3**

α-Fe_2O_3		Decomposition product	
d/Å	*I* (%)	*d*/Å	*I* (%)
2.700	100	2.710	100
2.519	70	2.512	80
2.207	20	2.251	30
1.841	40	1.845	50
1.694	45	1.685	40
1.454	30	1.452	30

Table 2. Powder X-ray diffraction analysis of the decomposition product of compound **5**

γ-Fe_2O_3		Decomposition product	
d/Å	*I* (%)	*d*/Å	*I* (%)
2.950	30	2.951	20
2.514	100	2.513	100
2.086	50	2.101	40

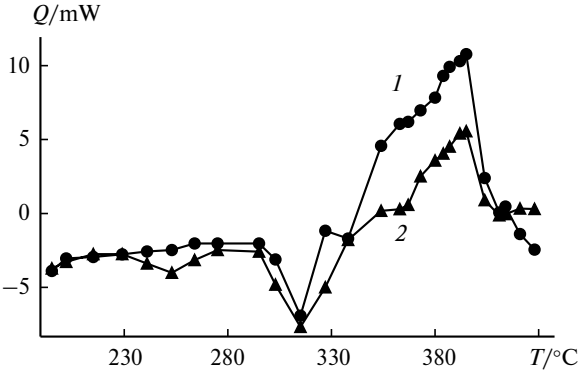

Fig. 6. Temperature dependence of the heat flow for complexes **3** (*1*) and **5** (*2*).

is indirect evidence that the formation of iron oxide from triangular cation **3** proceeds through the formation of a structure with a hexanuclear core observed in neutral cluster **5**. These processes are analogous to those observed earlier in the gaseous phase[2,3] and solution.[3]

Tetranuclear dianionic iron(III) pivalates

The partial replacement of potassium trimethylacetate in the starting reaction system with Me_3CCOOH ($FeSO_4 \cdot 7H_2O : KOOCCMe_3 : HOOCCMe_3 = 1 : 2 : 0.5$; EtOH; in air) afforded the polymeric complex $[K_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(H_2O)_2]_n$ (**7**) (50% yield), which was isolated as brown crystals after recrystallization from hexane.

The molecule of compound **7** consists of the alternating cluster dianions $Fe_4(O)_2(OOCCMe_3)_{10}^{2-}$ ($\{Fe_4\}^{2-}$) and the dinuclear $K_2(HOOCCMe_3)_2(H_2O)_2$ fragments linked to each other *via* the bridging carboxylate groups to form a chain (Fig. 7).

The tetranuclear dianionic fragment $\{Fe_4\}^{2-}$ (Fig. 8) contains iron atoms located in a single plane as a distorted rhombus; the metal atoms are located at nonbonded distances (Fe...Fe forming the sides of the rhombus are 3.332(4) and 3.314(4) Å ; the axial Fe...Fe distances are 2.942(4) and 5.959(4) Å). The metal atoms in the triangles involved in the rhombus are linked to each other *via* two tridentate-bridging oxygen atoms (Fe—O, 1.919(8), 1.926(8), and 1.872(8) Å) and eight bridging Me_3CCOO groups (Fe—O, 2.021(9)—2.093(9) Å). The oxygen atoms of the oxo groups deviate from the Fe_4 plane by 0.435 Å. The octahedral coordination environment of the iron atoms located on the long diagonal of the rhombus involves also two trimethylacetate groups (Fe—O, 1.940(9) Å). The latter serve as bridges between the iron and potassium atoms and link the tetranuclear iron and dipotassium fragments (K—O, 2.762(12) Å) as well as the potassium atoms in the dipotassium fragment (K—O, 2.669(11) Å).

Like polynuclear iron(III) complexes **4** and **5**, compound **7** exhibits antiferromagnetic properties, and its magnetic moment decreases from 4.19 to 1.17 μ_B in a 300—2 K temperature range (Fig. 9).

Decomposition of complex **7** started above 75 °C (Fig. 10), the process being highly endothermic (endotherm has a complex shape). In the first step (75—110 °C), the weight loss was 2.8±0.5%. At 110 °C, violation of monotonicity is observed in the temperature dependence of the heat flow. Apparently, the water molecules are eliminated in this temperature range (percentage of H_2O in molecule **7** is 2.3%). In a temperature range of 110—220 °C, 13.2±1.0% of the weight was additionally lost in two steps, the process being accompanied by a large endotherm. Presumably, the hydroxo groups were deprotonated, the ligand environment of the iron atoms changed, and two Me_3CCOOH molecules were removed (in molecule **7**, two moles of trimethylacetic acid account for 12.91%) in this temperature range. At temperatures above 240 °C, the compound underwent further decomposition accompanied by an endotherm and a rather extensive weight loss. In the final step of thermal decomposition, a large amount of energy was released. The total weight loss in the temperature range under study was 74.0±1.5% (weight of the solid residue was 26%). Powder X-ray diffraction study demonstrated that decomposition gave poorly crystallized potassium ferrite $KFeO_2$ (Table 3). The calculated amount of $KFeO_2$ is 26.14%.

Recrystallization of complex **7** from MeCN afforded bright-brown crystals of the $K_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(MeCN)_2$ compound (**8**). X-ray diffraction study demonstrated that the tetranuclear $\{Fe_4\}^{2-}$ dianion in molecule **8** remains intact, but the ligand environment of the Fe atoms is rearranged (Fig. 11). The geometry of the $Fe_4(\mu_3\text{-}O)_2$ core changes only slightly. The metal atoms in the octahedral environment formed by oxygen atoms are located virtually in a single plane and form a distorted rhombus with Fe...Fe nonbonded distances (Fe...Fe forming the sides of the rhombus are 3.287(4), 3.295(4), 3.408(4), and 3.422(4) Å; the axial Fe...Fe distances are 3.003(4) and 5.997(4) Å). The tridentately coordinated oxygen atoms (Fe—O, 1.852(8)—2.020(10) Å) are located above and below the metal core. Unlike the dianion in complex **7**,

Table 3. Powder X-ray diffraction analysis of the decomposition products of compounds **7** and **8**

$KFeO_2$		Decomposition product of **7**		Decomposition product of **8**	
d/Å	*I* (%)	*d*/Å	*I* (%)	*d*/Å	*I* (%)
2.846	100	2.865	40	2.855	100
2.690	10	2.705	5	2.695	20
2.577	15	2.557	7	2.583	25
2.455	10	2.463	4	2.458	25
2.227	10	2.267	4	2.236	25

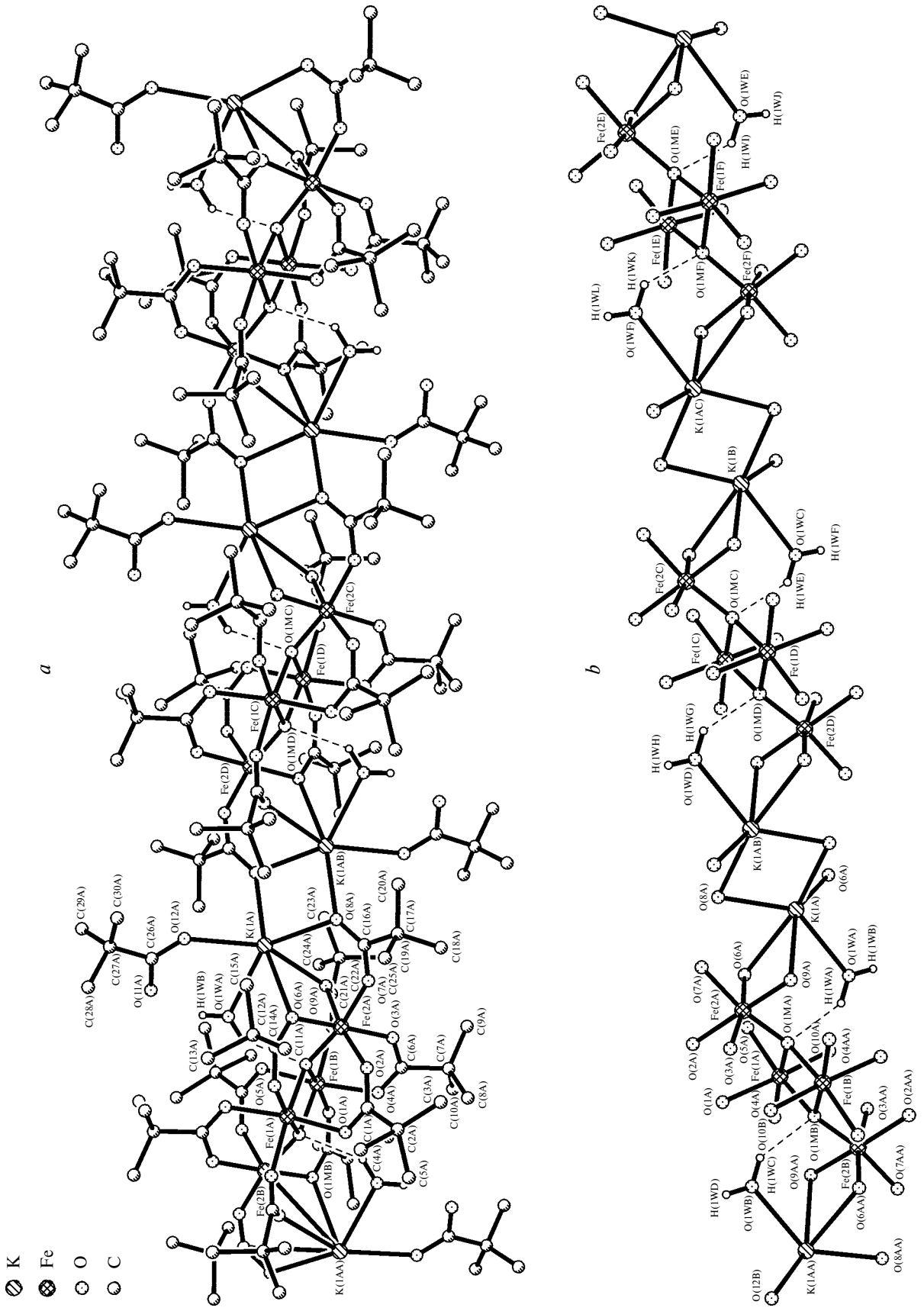

Fig. 7. Structures of the supramolecular polymer chain (*a*) and the metal-oxygen core (*b*) of complex **7**.

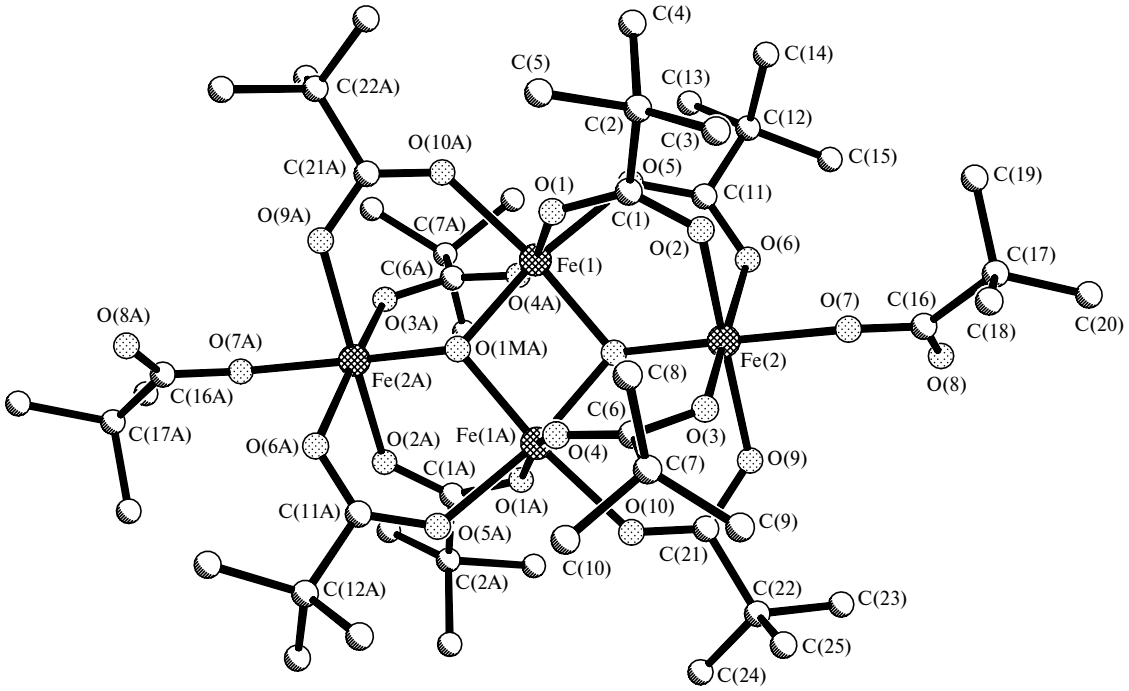

Fig. 8. Structure of the tetranuclear iron-containing fragment of complex **7**.

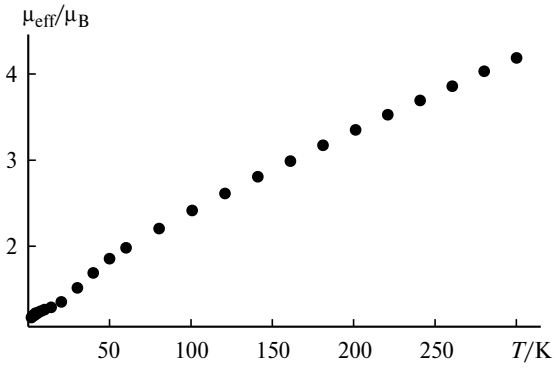

Fig. 9. Magnetic properties of complex **7**.

the $\{Fe_4\}^{2-}$ dianion of compound **8** contains only six bridging trimethylacetate groups, *via* which the iron atoms are linked (Fe—O, 2.023(10)—2.111(10) Å), whereas two other carboxylate groups are chelating (Fe—O, 2.102(10)—2.152(8) Å) and are bound to the peripheral iron atoms. Each K atom is linked to the $\{Fe_4\}^{2-}$ dianion *via* contacts with one O atom of the bridging oxo group (K—O, 2.796(11) Å), one O atom of the chelating trimethylacetate group (K—O, 2.838(10) Å), and one O atom of the bridging trimethylacetate group (K—O, 2.740(12) Å). The latter group serves as a bridge between the central and peripheral Fe^{III} atoms. The coordination environment of K atoms involves also one Me_3CCOOH molecule (K—O, 2.787(13) Å) and one MeCN molecule (K—N, 2.888(19) Å) (see Fig. 11), and the coordination number of K atoms is 6. As a result, antiferromagnetic compound **8** (μ_{eff} = 5.56 μ_B (300 K)—0.18 μ_B (4.6 K), Fig. 12) exists as a discrete supramolecular assembly, unlike molecule **7** existing as a polymeric supramolecular chain.

The structurally similar discrete supramolecular structures containing sodium ions, *viz.*, $Na_2Fe_4(O)_2(OOCCMe_3)_{10}(MeCN)(Me_2CO)$ (**9**) and $Na_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2 \cdot 4CH_2Cl_2$ (**10**), have been synthesized recently[1] from the hexanuclear complex $Fe_6(O_2)(O)_2(OOCCMe_3)_{12}(HOOCCMe_3)_2$.

The decomposition process of compound **8** (see Fig. 10) is analogous to that observed for complex **7**. In a temperature range of 75—125 °C, the weight loss was 5.0±1.0% (percentage of acetonitrile in molecule **8** was 5.03%), the process being accompanied by an endotherm. In a temperature range of 130—230 °C, 12.5±1.0% of the weight was lost, the endothermic process occurring in two steps (percentage of Me_3CCOOH in molecule **8** was 12.51%). At temperatures above 240 °C, the resulting product decomposed.

The character of the energy changes during decomposition of compound **7** at temperatures above 240 °C is identical to that observed for compound **8** (Fig. 13). For compound **8**, the weight loss in the temperature range under study was 73.5±2.0%, and the weight of the solid residue was 26.5%, which corresponds, as in the case of complex **7**, to mixed oxide $KFeO_2$ (see Table 3). However, this oxide is well crystallized. The calculated amount of $KFeO_2$ is 25.40%. The probability of the presence of

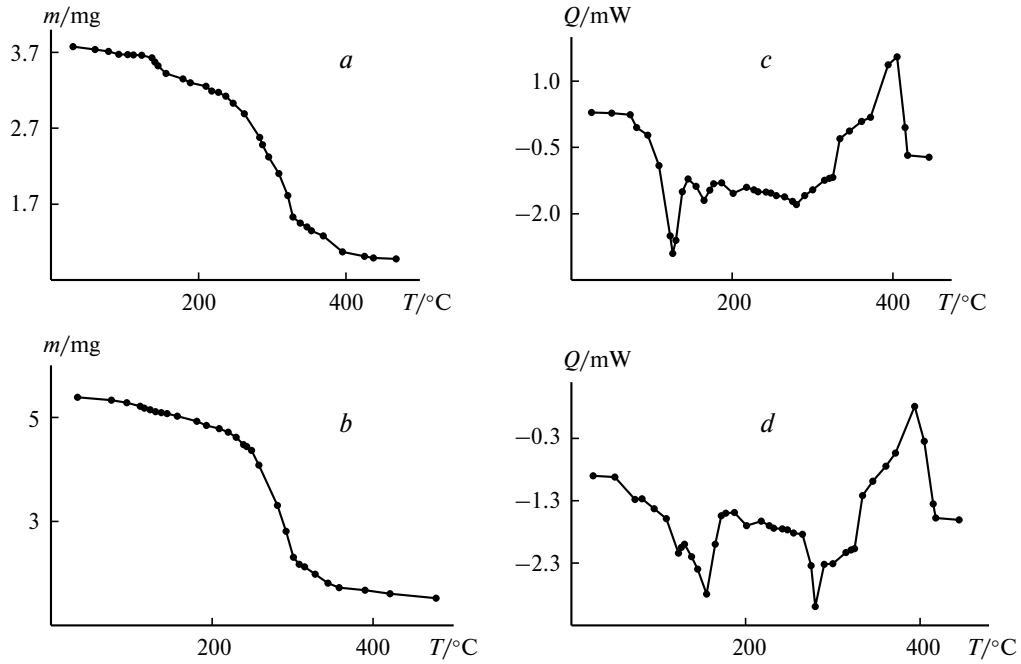

Fig. 10. Characteristics of thermolysis of complexes **7** and **8**: the integral dependence of the change in the weight on the temperature for complexes **7** (*a*) and **8** (*b*); the temperature dependence of the heat flow for **7** (*c*) and **8** (*d*).

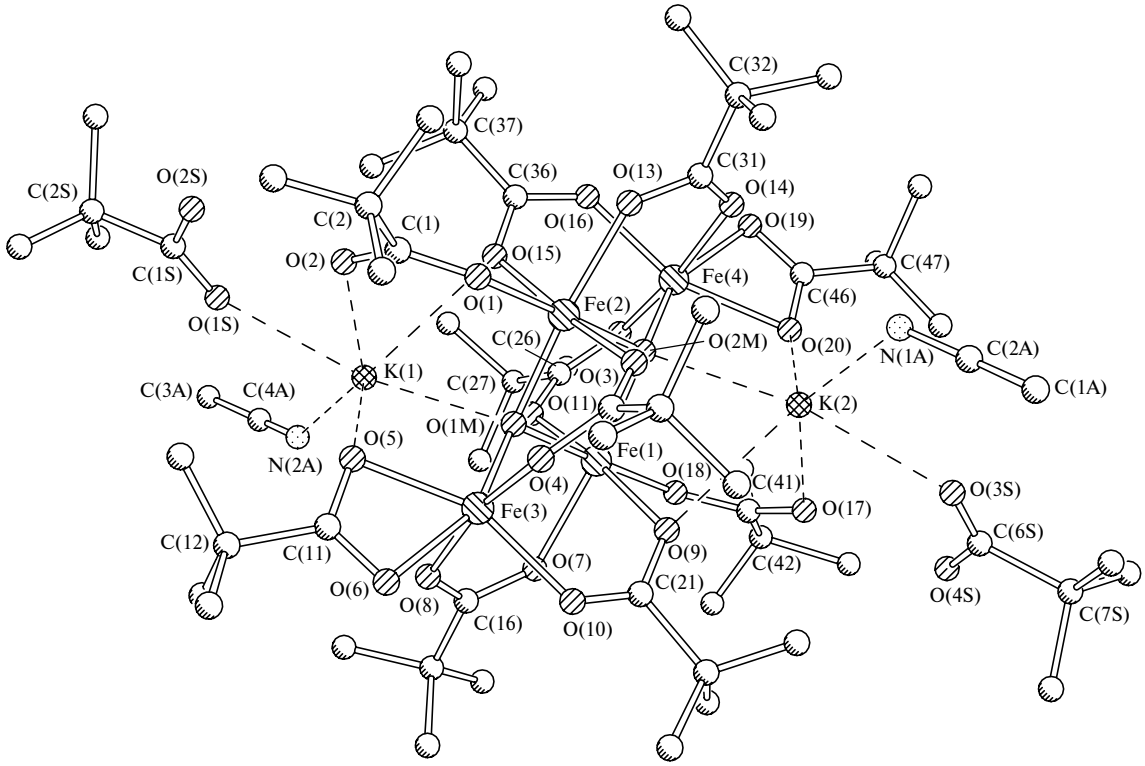

Fig. 11. Structure of complex **8**.

compounds with compositions other than $KFeO_2$ among decomposition products of complexes **7** and **8** is at most 4 wt.%.

The results of the present study provide an explanation for the general scheme of transformations of iron-containing complexes. In the first step, the reaction in the

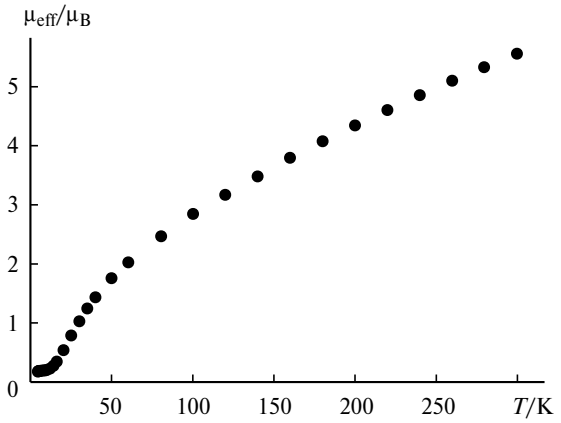

Fig. 12. Magnetic properties of complex **8**.

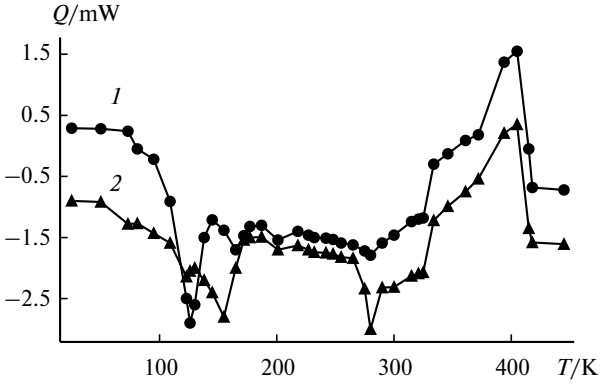

Fig. 13. Temperature dependence of the heat flow for complexes **7** (*1*) and **8** (*2*).

$FeSO_4 \cdot 7H_2O$—$KOOCCMe_3$ system affords, apparently, the trinuclear $[Fe_3(\mu_3\text{-}OH)(\mu_2\text{-}OOCCMe_3)_6L_3]^-$ anion (L = H_2O or Me_3CCOOH depending on the presence of trimethylacetic acid), which is oxidized to give the trinuclear $[Fe_3O(OOCCMe_3)_6(H_2O)_3]^+$ cation. Under more drastic conditions, the latter can be transformed into hexanuclear complex **5**. In the presence of Me_3CCOOH as a component of the reaction mixture, the trinuclear cation can also give tetranuclear complexes, as evident from the mass-spectrometric data.[2,3] However, in this case, the presence of water molecules bound to potassium atoms is an important factor of structure formation. The presence of water molecules is favorable for the formation of a polymer chain, because the protons of H_2O are involved in hydrogen bonding with the oxygen atoms of the Fe_3O fragments (O...O, 2.996(11) Å), thus preventing them from being involved in other interactions, whereas the replacement of the water molecules with acetonitrile molecules, which cannot be involved in hydrogen bonding, results in the formation of K...OFe_3 contacts and the transformation of the structure into a discrete supramolecular system.

Experimental

All operations associated with the synthesis of new complexes were carried out in freshly distilled solvents in air. Commercial reagents $FeSO_4 \cdot 7H_2O$ (special purity grade), KOH (reagent grade), and trimethylacetic acid (Fluka) were used. The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The static magnetic susceptibilities χ'_m were measured at the International Tomography Center of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk) on a SQUID-MPMS-5S Quantuim Design magnetometer in a 2—300 K temperature range. The effective magnetic moments were calculated by the equation[9]

$$\mu_{eff} = (8\chi'_m T)^{1/2}.$$

Thermal decomposition of compounds **3**, **5**, **7**, and **8** was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on DSC-20 and TG-50 units of the TA-3000 thermoanalyzer (Mettler). In all experiments, samples were heated under dry argon at a constant rate of 5 K min^{-1}. Four DSC experiments and three TGA experiments were carried out for each compound. The weight loss during thermal decomposition was determined directly on a TG-50 unit; the accuracy of the weighing device was $\pm 2 \cdot 10^{-3}$ mg. Thermal decomposition was also studied in steps by DSC, the temperature range of investigation being divided into intervals. The width and number of these intervals were determined based on the preliminary general information on the changes in the weight and energy during decomposition. This method of performing experiments allowed us to determine the weight loss in each temperature interval and compare the results obtained by DSC and TGA. A satisfactory agreement between the results obtained by two methods confirmed the reliability of the data. The anomalous points and the thermal effects in the thermograms were determined with an accuracy of ±1° and ±0.5%, respectively.

Powder X-ray diffraction analysis of decomposition products was carried out on a FR-552 monochromator chamber (Cu-Kα1 radiation) using germanium as the internal standard (X-ray diffraction patterns were measured on an IZA-2 comparator with an accuracy of ±0.01 mm) and a STOE Powder Diffraction System.

Oxotris(η^1-aquo)hexakis(μ_2-trimethylacetato-*O*,*O*′)triiron(III) trimethylacetate, solvate with ethanol, $[Fe_3O(OOCCMe_3)_6(H_2O)_3]^+(OOCCMe_3)^- \cdot 3C_2H_5OH$ (3). ***A.*** Ethanol (20 mL) was added to weighed samples of $FeSO_4 \cdot 7H_2O$ (1.50 g, 5.4 mmol) and $KOOCCMe_3$ (2.27 g, 16.2 mmol). The brown reaction mixture was stirred at 50 °C for 30 min and then filtered off from the precipitate of K_2SO_4 that formed. The resulting solution was concentrated to 5 mL and kept at ~20 °C for 20 h. Brown prismatic crystals suitable for X-ray diffraction study were separated from the solution by decantation and washed with cold EtOH. The yield was 0.68 g (35%). Found (%): C, 45.1; H, 7.9. $C_{41}H_{87}Fe_3O_{21}$. Calculated (%): C, 45.44; H, 8.09. IR, ν/cm^{-1}: 3374 br.m, 2980 s, 2960 s, 2932 s, 2904 m, 2872 m, 1708 m, 1664 m, 1592 s, 1484 s, 1456 w, 1424 s, 1364 m, 1228 s, 1176 m, 1088 w, 1040 m, 1022 m, 940 w, 900 w, 868 w, 788 m, 748 w, 608 s, 448 s.

B. Ethanol (15 mL) was added to weighed samples of $FeCl_3 \cdot 6H_2O$ (1.00 g, 3.7 mmol) and $KOOCCMe_3$ (1.55 g,

11.1 mmol). The reaction mixture was stirred at 80 °C and then filtered off from the precipitate of KCl that formed. The resulting brown solution was concentrated to 5 mL and cooled to ~20 °C. After 24 h, brown prismatic crystals of complex **3** were separated from the solution by decantation and washed with cold EtOH. The yield was 0.93 g (70%). Found (%): C, 45.2; H, 7.9. $C_{41}H_{87}Fe_3O_{21}$. Calculated (%): C, 45.44; H, 8.09. IR, ν/cm^{-1}: 3374 br.m, 2980 s, 2960 s, 2932 s, 2904 m, 2872 m, 1708 m, 1664 m, 1592 s, 1484 s, 1456 w, 1424 s, 1364 m, 1228 s, 1176 m, 1088 w, 1040 m, 1022 m, 940 w, 900 w, 868 w, 788 m, 748 w, 608 s, 448 s.

Bis(μ$_3$-oxo)bis(μ$_2$-hydroxo)dodecakis(μ$_2$-trimethylacetato-*O*,*O*′)(η^1-tetrahydrofuran)(η^1-trimethylacetic acid)hexairon(III), solvate with benzene, $[Fe_6(O)_2(OH)_2(OOCCMe_3)_{12}(HOOCCMe_3)(THF)]\cdot 1.5C_6H_6$ (5). Benzene (20 mL) and THF (0.5 mL) were added to weighed samples of $FeSO_4\cdot 7H_2O$ (1.00 g, 3.6 mmol) and $KOOCCMe_3$ (1.51 g, 10.8 mmol). The reaction mixture was stirred at 60 °C for 1 h until the solution turned black-brown. The resulting solution was filtered, concentrated to 5 mL, and cooled to 5 °C. After 18 h, dark-brown crystals of complex **5** suitable for X-ray diffraction study precipitated. The crystals were separated by decantation and washed with cold benzene. The yield was 0.47 g (50%). Found (%): C, 49.3; H, 7.2. $C_{78}H_{137}Fe_6O_{31}$. Calculated (%): C, 49.15; H, 7.24. IR, ν/cm^{-1}: 2964 s, 2928 s, 2872 m, 1696 w, 1660 w, 1604 s, 1596 s, 1560 s, 1552 s, 1536 s, 1504 m, 1484 s, 1460 w, 1424 s, 1380 s, 1360 s, 1312 v.s, 1228 s, 1096 v.s, 1048 v.s, 1032 w, 936 s, 900 s, 816 s, 788 m, 696 m, 680 s, 604 m, 520 w, 440 m.

Bis(μ$_3$-oxo)hexakis(μ$_3$-trimethylacetato-*O*,*O*,*O*′)tetrakis(μ$_2$-trimethylacetato-*O*,*O*′)bis(η^1-aquo)bis(η^1-trimethylacetic acid)dipotassiumtetrairon(III), $[K_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(H_2O)_2]_n$ (7). Ethanol (35 mL) was added to weighed samples of $FeSO_4\cdot 7H_2O$ (1.00 g, 3.6 mmol), $KOOCCMe_3$ (1.01 g, 7.2 mmol), and $HOOCCMe_3$ (0.18 g, 1.8 mmol). The reaction mixture was stirred at 50 °C for 10—15 min until the solution turned black-brown. Then the solution was filtered off from the suspension that formed, concentrated to dryness, and dissolved in hexane (15 mL). The dark-brown solution was filtered and kept at ~20 °C for 50 h. Brown crystals of complex **7** were separated from the solution by decantation and washed with cold hexane. The yield was 0.71 g (50%). Found (%): C, 45.4; H, 7.2. $C_{60}H_{112}K_2Fe_4O_{28}$. Calculated (%): C, 45.52; H, 7.13. IR, ν/cm^{-1}: 3444 m, 2976 s, 2960 s, 2932 s, 2868 m, 1728 m, 1716 m, 1620 m, 1600 m, 1572 s, 1552 s, 1520 m, 1484 s, 1456 m, 1416 s, 1376 m, 1364 m, 1356 m, 1224 m, 1176 w, 1028 v.s, 1032 w, 936 v.s, 892 w, 864 v.s, 792 m, 748 v.s, 676 w, 652 m, 604 s, 564 m, 544 m, 428 s.

Bis(μ$_4$-oxo)tetrakis(μ$_3$-trimethylacetato-*O*,*O*,*O*′)tetrakis(μ$_2$-trimethylacetato-*O*,*O*′)bis(η^2-trimethylacetato)bis(η^1-acetonitrile)bis(η^1-trimethylacetic acid)dipotassiumtetrairon(III), $K_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(MeCN)_2$ (8). A weighed sample of complex **7** (0.50 g, 0.32 mmol) was dissolved in MeCN (15 mL) at 80 °C. The reaction solution was kept at ~20 °C for 1 h, after which dark-brown crystals of complex **8** precipitated. The yield was 0.37 g (70%). Found (%): C, 47.3; H, 7.0. $C_{64}H_{116}K_2Fe_4N_2O_{26}$. Calculated (%): C, 47.12; H, 7.17. IR, ν/cm^{-1}: 3532 m.br, 3484 m, 2964 s, 2932 s, 2868 m, 1784 w, 1732 m, 1704 m, 1672 m, 1580 s, 1536 m, 1484 s, 1420 s, 1376 m, 1360 m, 1296 m, 1228 m, 1192 m, 1028 w, 940 w, 912 w, 868 w, 816 w, 792 m, 760 w, 652 m, 612 m, 564 w, 504 w, 432 m.

X-ray diffraction study of complexes 3, 5, 7, and 8. X-ray diffraction studies were carried out at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) on a Bruker AXS SMART 1000 diffractometer[20—22] equipped with a CCD detector (Mo-Kα, graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 60°$).

The structures of all complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacements parameters for all nonhydrogen atoms. The hydrogen atoms of the *tert*-butyl substituents in the trimethylacetate ligands of complexes **3**, **5**, and **8** were placed in

Table 4. Crystallographic parameters for complexes **3**, **5**, **7**, and **8**

Parameter	**3**	**5**	**7**	**8**
Molecular formula	$C_{41}H_{87}Fe_3O_{21}$	$C_{78}H_{137}Fe_6O_{31}$	$C_{60}H_{114}K_2Fe_4O_{28}$	$C_{64}H_{116}K_2Fe_4N_2O_{26}$
Space group	*P*-31*c*	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a/Å	12.543(6)	13.815(2)	13.456(8)	14.941(3)
b/Å	12.543(6)	15.326(3)	13.984(8)	22.285(4)
c/Å	23.032(8)	25.863(4)	14.460(9)	26.548(4)
α/deg	90	91.151(3)	113.49(4)	90
β/deg	90	94.974(3)	107.16(4)	90
γ/deg	120	114.570(3)	108.12(4)	90
V/Å^3	3138(2)	4951.8(14)	2080(2)	8840(2)
Z	2	2	1	4
ρ_{calc}/g cm^{-3}	1.098	1.280	1.266	1.226
μ/cm^{-1}	7.74	9.26	8.53	8.03
Number of measured reflections	6712	19434	5173	18279
Number of reflections with $I > 4.0\sigma$	2746	14483	4857	12990
R_1	0.0586	0.0780	0.0722	0.0771
wR_2	0.1212	0.2088	0.1982	0.1162

calculated positions and refined using a riding model. The hydrogen atoms of the hydroxo groups of the coordinated trimethylacetic acid molecules in complexes **3**, **5**, and **8** were revealed from difference Fourier syntheses and refined isotropically. Calculations were carried out using the SHELX97 program package.[20] The crystallographic parameters and details of the structure refinement are given in Table 4.

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