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The issue is dedicated to the 70th birthday of Academician V.I. Ovcharenko

Synthesis and Structure of Iron(III) Malonates with Rubidium and Cesium Cations

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Abstract—New coordination compounds of iron(III) with malonic acid (H_2Mal) dianions and rubidium $[Rb_3Fe(Mal)_3(H_2O)]_n$ (**I**) and cesium $[Cs_3Fe(Mal)_3(H_2O)]_n$ (**II**) cations are synthesized. According to the X-ray diffraction data (CIF files CCDC nos. 2125054 (**I**) and 2125055 (**II**)), the crystalline compounds are isostructural 3D coordination polymers in which the repeated structural unit is the tetranuclear block $[M^I_3Fe(Mal)_3(H_2O)]$ (M^I = Rb (**I**) or Cs (**II**)) consisting of the central tris-chelate fragment $\{Fe(Mal)_3\}^{3-}$ linked by the malonate bridges with the Rb or Cs ions.

Keywords: coordination polymers, iron(III), dicarboxylic acids, malonic acid, X-ray diffraction

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INTRODUCTION

Carboxylate coordination compounds of iron(III) are of great interest for researchers due to diverse and sometimes nontrivial properties of these objects. Their magnetic characteristics, catalytic activity, and biological properties are widely studied [1–5]. Many of the known compounds of this type, for example, compounds with ions Li–Fe, Fe–Mn, Fe–Co, Fe–Ni, Fe–Zn, etc., are promising for the purposeful synthesis of complex oxides and often can act as precursors for their preparation, including those in the form of nanoparticles suitable for manufacturing magnetic or cathodic materials [6–9].

However, the understanding of possibilities of the known methods for assembling polynuclear heterometallic complexes with metal ions different in nature and the determination of their structures still remain to be an important stage in the development of this area of the chemistry of iron(III) compounds. In this case, the obtained information makes it possible to determine routes for the directed transformation of these complicated architectures into complex oxides with a certain arrangement of the ions in the solid phase (crystals, films, coatings, and others), which predetermines, as a rule, the properties of the final material [10, 11]. In this situation, one can use the methodologies known in chemistry that make it possible to perform rather purposeful control of assembling polynuclear and polymeric compounds. The use of polydentate ligands, such as dicarboxylic acids, in the synthesis of heterometallic 3*d*–*s* compounds provides polymeric systems of various dimensionality, including porous coordination polymers interesting from the viewpoint of gas sorption and separation, heterogeneous catalysts, or sensors [12–14]. It is known that the transition metal compounds with malonic acid anions and *s*-metal atoms are polymeric [15, 16]. The malonate dianions in the compounds with divalent metals form the bis-chelate fragment [7, 17], whereas the fragments are tris-chelate in the iron(III) compounds [18, 19]. In some cases, this tendency is retained on going to the substituted analogs of malonic acid [20–29]. The formation of the tris-chelate fragments with the anions of substituted malonic acids was also described for chromium(III) [30]. Malonates and their substituted analogs can coordinate to metal atoms to form six-membered chelate rings and exhibit the bridging function only in the case of both heterometallic and homometallic compounds [31–33], which is mainly related to the nature of the metal center. The formation of the bis-chelate fragments can be observed in the case of dicarboxylic acids and also for aromatic monocarboxylic acids bearing a donor substituent in the *ortho* position to the carboxyl group. For example, diiodosalicylic acid anions form the bis-chelate fragment with copper(II) atoms [34], whereas the monodentate mode of anion coordination is observed in the case of zinc(II) atoms [35, 36].

However, only several iron(III) compounds are known among a large scope of coordination compounds of 3*d* metals with the anions of malonic acid and its substituted analogs [7, 18, 19, 37]. Heterometallic complexes of *d* metals with rubidium and cesium ions are described by single examples, including copper(II) malonates with rubidium or cesium ions [38], and two cobalt(II) dimethylmalonates with cesium ions [20].

In this work, we present the results on the synthesis of the iron(III) coordination compounds with malonic acid anions and rubidium and cesium cations: $[M_3Fe(Mal)_3(H_2O)]_n$ (M = Rb (**I**) or Cs (**II**)). Their structures were studied, and the influence of alkaline metal ions on the molecular and crystal structures of new compounds was analyzed.

EXPERIMENTAL

All procedures on the synthesis of the compounds were carried out in air using distilled water and the following commercially available reagents: $FeCl_3 \cdot 6H_2O$ (reagent grade, Reakhim), malonic acid (H_2Mal, 99%, Fluka), Rb_2CO_3 (99.9%, Lankhit), and Cs_2CO_3 (99.9%, Lankhit).

The IR spectra of the synthesized compounds were recorded on a Perkin Elmer Spectrum 65 spectrometer equipped with a Quest ATR Accessory (Specac) instrument using the attenuated total reflection (ATR) mode in a range of 400–4000 cm^{-1}.

Synthesis of $[Rb_3Fe(Mal)_3(H_2O)]_n$ (I). Malonic acid (1.5 mmol, 0.1561 g) was dissolved in H_2O (10 mL), and Rb_2CO_3 (1.5 mmol, 0.3464 g) and then a solution of $FeCl_3 \cdot 6H_2O$ (0.5 mmol, 0.1351 g) in H_2O (10 mL) were added. The obtained light green solution was stirred for 30 min, filtered, and left to evaporate slowly in air. Green crystals suitable for X-ray diffraction (XRD) analysis were formed in 10 days.

IR (ATR, ν, cm^{-1} (m = medium, w = weak)): 3395 w, 1602 m, 1518 w, 1506 w, 1478 w, 1360 m, 1303 m, 1202 w, 959 w, 926 m, 800 w, 717 m, 636 w, 540 w, 444 w.

Synthesis of $[Cs_3Fe(Mal)_3(H_2O)]_n$ (II) was carried out using the procedure similar to that for compound **I** except for the use of Cs_2CO_3 (1.5 mmol, 0.4887 g) instead of Rb_2CO_3.

IR (ATR, ν, cm^{-1}): 3398 w, 1595 s, 1356 s, 1303 m, 1200 m, 958 m, 924 m, 797 w, 713 s, 636 w, 604 w, 536 m, 458 m, 438 m.

XRD of single crystals of compounds **I** and **II** was carried out using a Bruker D8 Venture diffractometer (MoK_α radiation, graphite monochromator, φ and ω scan modes). A semiempirical absorption correction was applied for compounds **I** and **II** using the SADABS program [39]. The structures were solved by a direct method and refined by least squares first in the isotropic approximation and then in the anisotropic approximation. The positions of the hydrogen atoms were calculated geometrically. All calculations were performed using the OLEX2 program [40]. The crystallographic characteristics and XRD experimental details are given in Table 1.

The coordinates of atoms and full crystalline parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2125054 (**I**) and 2125055 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

The reaction of $FeCl_3 \cdot 6H_2O$, malonic acid, and rubidium or cesium carbonate affords isostructural coordination compounds $[M^I_3Fe(Mal)_3(H_2O)]_n$ (M^I = Rb (**I**) or Cs (**II**)) that crystallize in the orthorhombic crystal system (space group *Pbcm*). The XRD data for the obtained samples showed a crystalline impurity and an amorphous phase, which we failed to identify.

Crystalline compounds **I** and **II** are three-dimensional coordination polymers in which three alkaline metal atoms, three malonic acid dianions, and one water molecule fall onto one iron(III) atom. The iron(III) atom exists in the octahedral environment formed by the oxygen atoms of three malonate anions to form the tris-chelate fragment (Fig. 1a). The Fe–O distances are 1.981(5)–2.022(5) and 1.980(2)–2.031(2) Å in compounds **I** and **II**, respectively. Two alkaline metal atoms coordinate eight oxygen atoms each, and one alkaline metal atom coordinates 11 oxygen atoms, including that from the water molecule. The Rb–$O(O_2CR)$ and Rb–$O(H_2O)$ distances are 2.930(5)–3.287(5) and 3.188(8)–3.239(8) Å, and the Cs–$O(O_2CR)$ and Cs–$O(H_2O)$ distances are 3.089(3)–3.439(2) and 3.294(4)–3.319(4) Å, respectively. The oxygen atoms of the water molecules are coordinated by three alkaline metal atoms and are additonally bound by hydrogen bonds to the oxygen atoms of the acid dianions (the O...O distance is 2.828(6) Å in **I** and 2.911(3) Å in **II**). The compound contains malonate anions of two types exhibiting the k^2, μ_7 coordination modes (O(1)/C(1)/C(2)/C(3)/O(3) dianion) and k^2, μ_9 coordination modes (O(5)/C(4)/C(5)/C(4)/O(5) dianion) (Fig. 1b).

The metal atoms of each type form parallel layers (Fig. 2). The distances between the metal ions in the layers are as follows: Rb...Rb 3.8432 Å, Cs...Cs 3.989 Å, and Fe...Fe 7.070 (**I**) and 7.132 Å (**II**). The distance between the planes is 3.571 Å in **I** and 3.761 Å in **II**. The density of the crystals is high: the packing coefficient is 88.6 in the rubidium complex and 87.8 in the complex with cesium.

As shown by an analysis of the CCDC, three iron(III) tris-malonate complexes have been

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_9H_8O_{13}FeRb_3$	$C_9H_8O_{13}FeCs_3$
FW	636.41	778.73
Crystal system	Orthorhombic	
Space group	*Pbcm*	
T, K	100	293
a, Å	14.2362(12)	14.4218(8)
b, Å	7.9061(6)	8.1305(5)
c, Å	14.2841(11)	15.0429(8)
V, Å^3	1607.7 (2)	1763.88(17)
Z	4	4
μ, mm^{-1}	10.03	7.02
Crystal size, mm	0.12 × 0.12 × 0.1	0.13 × 0.12 × 0.09
$T_{\min}$, $T_{\max}$	0.097, 0.381	0.208, 0.381
Number of measured reflections	11527	17151
Number of independent reflections	1651	2432
Number of reflections with $I > 2\sigma(I)$	1538	2240
R_{int}	0.086	0.032
$(\sin\theta/\lambda)_{\max}$, Å^{-1}	0.617	0.682
$R(F^2 > 2\sigma(F^2))$	0.052	0.022
$wR(F^2)$	0.135	0.053
S	1.14	1.14
Number of refined parameters	125	130
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	2.45/–1.10	0.82/–0.75

described to date. One of them has the molecular structure (in the composition of $[Co(NH_3)_6][Fe(Mal)_3]$ salt [18]), and two others have the structures of heterometallic coordination polymers with sodium $\{Na_6[Fe(Mal)_3]_2{\cdot}8H_2O\}_n$ and sodium and barium $\{NaBa[Fe(Mal)_3]{\cdot}3H_2O\}_n$ [19]. Interestingly, the $\{Fe(Mal)_3\}^{3-}$ fragments have the same structures in all cases, where the iron polyhedron represents an almost ideal octahedron and the Fe–O distances are 1.957–2.030 Å. The structures of the described [19] heterometallic complexes are different. In the polymeric iron(III) complex with sodium and barium, one sodium atom, one barium atom, three malonate ligands, and three water molecules fall onto one iron(III) atom. In the heterometallic iron(III)–sodium polymer, the iron to sodium ratio is 1 : 3 as in the synthesized compounds **I** and **II**. However, the complex with sodium ions contains eight water molecules, whereas complexes **I** and **II** contain one water

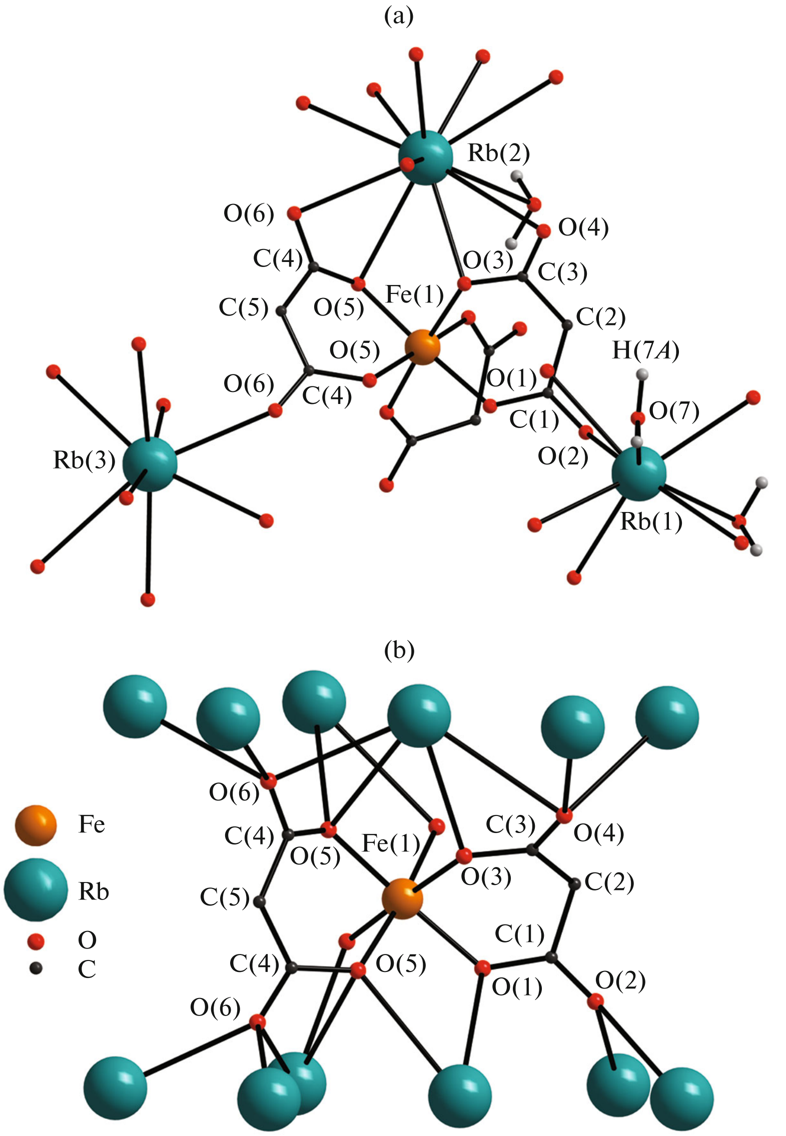

Fig. 1. Fragment of compound **Ia** and two structurally independent anions in compound **Ib** (hydrogen atoms are shown only for water molecules).

molecule coordinated to one of the alkaline metal atoms, which somewhat changes the geometry of the polymer and complicates the system of hydrogen bonds, but exerts no significant effect on the three-dimensional structure of the polymer similarly to the heterometallic complexes studied by us. However, unlike compounds **I** and **II**, the layers of metal atoms in the iron(III)–sodium complex are not planar but are slightly corrugated, which impedes the estimation of the distance between them. An analysis of the three-dimensional structure of the iron(III)–sodium–barium coordination polymer shows that the metal layers can also be distinguished in the crystal of this compound, but one of them is heterometallic being formed by the iron and sodium ions, and another layer is homometallic: formed by the barium ions only.

The coordination compounds of iron(III) with malonic acid anions and rubidium and cesium cations were synthesized in this work. The cation radius (1.66 Å for Rb^+, 1.88 Å for Cs^+) was shown to exert no effect on the structures of the products. The both compounds contain the layers of the tris-chelate iron(III) fragments linked by the alkaline metal atoms to form the 3D polymeric structure.

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The XRD and IR spectroscopic studies were carried out using the equipment of the JRC PMR IGIC RAS.

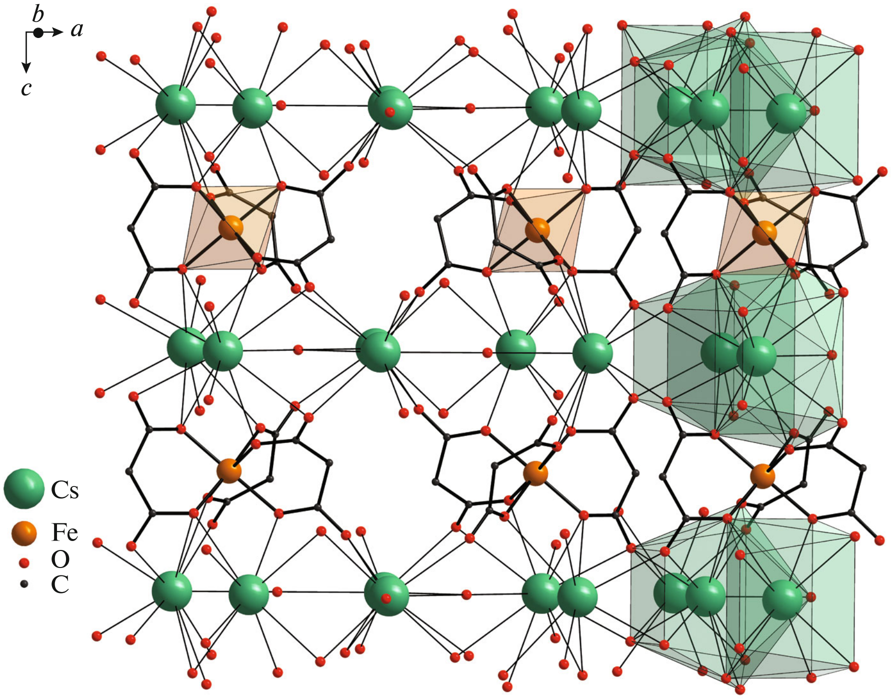

Fig. 2. Fragment of compound **II** (hydrogen atoms are omitted).

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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