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**SYNTHESIS AND STRUCTURAL STUDIES OF
HETEROMETALLIC
{[FeCa₂(Sal)₂(SalH)₃(DMA)₂(CH₃OH)₂]}_n
SALICYLATE COMPLEX**

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SYNTHESIS AND STRUCTURAL STUDIES OF HETEROMETALLIC $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$ SALICYLATE COMPLEX

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Abstract. A new heterometallic iron(III) compound, derivative of salicylic acid, catena-poly[bis(methanol)-bis(*N,N*-dimethylacetamide)-tris(μ -salicylato)-bis(μ -salicyl)-dicalcium(II) iron(III)], has been synthesized and characterized by infrared spectroscopy, single-crystal X-ray diffraction and elemental analysis. Single-crystal X-ray diffraction study revealed that the synthesized compound forms an 1D coordination polymer with general formula $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$ (**1**). The compound **1** crystallizes in the $P2_1/c$ space group of the monoclinic system with the following unit cell parameters: $a=9.76785(9)$, $b=37.3386(4)$, $c=13.82575(12)$ Å, $\beta=103.6421(9)^\circ$, $Z=4$. The independent part of the unit cell contains one iron and two calcium ions, in which the iron(III) ion has an octahedral coordination sphere. The different coordination modes of the five molecules of salicylic anions revealed by IR analysis were confirmed by X-ray studies, showing that the salicylate anions play the role of bridging ligands and coordinate in three different ways, thus the carboxylic group forms bridges through three different coordination pathways, namely: bidentate, tridentate and pentadentate fashion.

Keywords: oxo-carboxylate, iron(III), calcium(II), heteronuclear cluster, salicylic acid, *s-d* metals.

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Introduction

The synthesis of transition metal clusters has attracted significant interest due to their relevance to many fields, including the nature of chemical bonds in complexes and the possibility of self-assembly in the crystal [1], luminescent properties [2], biological properties [3,4], molecular magnetism [5,6], catalysis [7] physiologically active agents [8,9] and bioinorganic chemistry.

Transition metal clusters have been synthesized and analysed as models for the active centres of many ferro-proteins, such as monooxygenase [10], ribonucleotide reductase [11], favouring the development of bioinorganic chemistry [12,13]. Bridged iron clusters formed by mono- and dibasic carboxylic acids have been widely investigated. However, there are few publications in the literature based on the synthesis and study of heteroatomic coordination compounds of iron with oxycarbonic acids, in particular with salicylic acid, especially investigated by the single crystal X-ray diffraction method.

Salicylic acid provides two strong donor centres and coordinates to metal ions in a variety of ways [14,15], thus forming coordination

compounds with diverse nuclearity [16,17]. Since salicylic acid can participate in coordination through one or both functional groups, a series of coordination compounds in which the ligand can coordinate in various ways [18,19]: monodentate [20], bidentate chelating [21], bridging bidentate ligand [22,23] and bridging- μ_3 and chelate coordination [24] are known. Coordination compounds of salicylic acid in which the hydroxyl ion of the carboxylic group remains deprotonated are very rarely encountered [23]. Salicylic acid is a well-studied compound, mainly due to its biological properties [25–28] and is widely used in various chemical reactions, in medicine and cosmetology. In coordination chemistry, a particular interest in salicylic acid is due to the carboxylic group that plays a significant role in the interaction with biologically important metal ions.

Drake, S.R. *et al.* initiated the study of the coordination chemistry of alkaline earth metals (Mg, Ca, Sr and Ba) in both aqueous and organic environments [29]. Mg and Ca are essential chemical elements for life forms, from a biological point of view being part of macroelements that are found in relatively large quantities in living organisms in the form of inorganic and organic

species and the role of regulating some physiological processes by these two metals consists in changing the metabolic reactions that take place inside and outside the cell and can be attributed to the atomic radii, and the charge of the atoms, which leads to the stability of the octahedron $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ present in many coordination compounds of magnesium. The same behaviour is observed in the case of calcium ion with a coordination number more than 6 (often with distorted stereochemistry). The synthesis and the molecular structure of the alkaline earth metal salicylates were established by single crystal X-ray diffraction, where calcium ions are hexa- and heptacoordinated [30]. Other heteronuclear Fe(III)-Ca(II) carboxylate clusters include the trinuclear $\{\text{Fe}_2\text{Ca}\}$ cluster of trichloroacetic acid with antiferromagnetic exchange [31], the tetranuclear $\{\text{Fe}_3\text{Ca}\}$ of pyridinedicarboxylic acid with antimicrobial activity [32] and the hexanuclear $\{\text{Fe}_4\text{Ca}_2\}$ cluster of dichloroacetic acid with antiferromagnetic interactions [33].

Analogue compounds containing $\{\text{FeSr}_2\}_n$ and $\{\text{FeCa}_2\}_n$ cores manifested biostimulating properties in the process of catalase biosynthesis in *Penicillium piceum* F-648 A3 and *Penicillium funiculosum* CNMN FD strains [8,9].

In continuation of previous results [24], within the current study, the synthesis of a new *s-d* heteronuclear coordination polymer with salicylic acid of iron(III) and calcium(II) metal ions is reported.

Experimental

Materials

The starting compound $\text{Ca}(\text{SalH})_2$ was prepared by the reaction of calcium oxide with salicylic acid [22]. All solvents and reagents such as salicylic acid, calcium(II) oxide, methanol, dimethylacetamide (DMA) were obtained from commercial sources.

Synthesis of

$\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$ (1)

The complex **1** was obtained according to the method described previously [24], shown in the Scheme 1, following the reaction between solutions of $\text{Ca}(\text{SalH})_2 \cdot n\text{H}_2\text{O}$ (6.56 g, 17.82 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.80 g, 4.45 mmol) in methanol (40 mL) with the subsequent addition of DMA (8 mL). The obtained solution was left for crystallization under ambient conditions. In one month, single crystals as dark red hexagonal prisms were obtained. The crystalline product was separated by filtration, washed with the solvent mixture ethanol:diethyl ether (1:1) and air dried. Yield: 1.02 g, 39% (based on iron). Elemental analysis was calculated for

$\text{C}_{45}\text{H}_{49}\text{N}_2\text{O}_{19}\text{FeCa}_2$ (1057.87 g/mol): C 51.09, H 4.67, N 2.65; found C 49.84, H 4.94, N 3.07%. IR (ν , cm^{-1}): 3609 sh, 3062 w, 2934 vw, 1618 sh, 1599 s, 1511 m, 1484 sh, 1458 vs, 1398 sh, 1374 m, 1325 w, 1248 s, 1192 vw, 1145 s, 1031 s, 967 w, 863 m, 760 vs, 703 s, 666 s, 600 w, 581 w, 536 m, 461 w, 434 m.

Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a GmbH Vario-EL-III-CHNOS elemental analyser at the Centre for physical and inorganic chemistry of the Institute of Chemistry.

IR spectra (4000–400 cm^{-1}) were registered with a Perkin-Elmer 100 FT-IR spectrometer at room temperature using ATR technique. Intensities are presented as: vs= very strong, s= strong, m= medium, w= weak, vw= very weak, and sh= shoulder.

Table 1

Crystallographic data, details of data collection, and structure refinement parameters for compound 1.

Parameters	Value
Empirical formula	$\text{C}_{45}\text{H}_{49}\text{Ca}_2\text{FeN}_2\text{O}_{19}$
Formula weight (g/mol)	1057.87
Space group	$P2_1/c$
<i>a</i> (Å)	9.76785(9)
<i>b</i> (Å)	37.3386(4)
<i>c</i> (Å)	13.82575(12)
α (°)	90
β (°)	103.6421(9)
γ (°)	90
Volume (Å ³)	4900.23(8)
Z	4
λ (Å)	1.5418
ρ_{calc} (g/cm ³)	1.434
Crystal size (mm ³),	0.10 × 0.05 × 0.02
Temperature (K)	100
μ (mm ⁻¹)	4.963
Reflections collected	36540
Independent reflections	8643 [$R_{\text{int}} = 0.0336$]
Data/ restraints/ parameters	8643/96/ 610
R_1	0.0595
wR_2	0.1557
GOF	1.039
Largest diff. peak/hole / e Å ⁻³	1.00/-0.99

X-ray crystallography Suitable crystals for single crystal X-ray diffraction study of $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$ coordination polymer were grown by slow evaporation of the solvent mixture CH_3OH -DMA. The intensity data were collected on an Oxford Diffraction Xcalibur Eos diffractometer. Data collection, cell refinement, and data reduction

were performed with CrysAlisPro (Oxford Diffraction) [34]. The structure was solved with ShelXT2014 [35] and was refined anisotropically for non-hydrogen atoms. Crystallographic data for complex **1**, CCDC-2334808 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures [36]. The crystallographic data and details of the structure refinement are shown in Table 1.

Results and discussion

The synthesis of the new hetero-trinuclear coordination polymer, with the composition $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$ (**1**), consists in the direct interaction of calcium(II) salicylate solution in methanol with iron nitrate(III) (4:1) according to the Scheme 1. The reaction was performed in CH_3OH -DMA solvent mixture system at ambient temperature. The obtained red crystalline compound is stable in air, soluble in organic solvents (DMA, DMF, DMSO, CH_3OH , $\text{C}_2\text{H}_5\text{OH}$).

The obtained monocrystalline compound was investigated by elemental analysis, Fourier-transform infrared spectroscopy (FTIR) and single crystal X-ray diffraction.

IR spectroscopic characterization

The IR spectrum of the compound **1** has been interpreted in comparison with the free salicylic acid (H_2Sal). The presence of carboxylic groups, phenolic ring, DMA, CH_3OH molecules and the $\{\text{FeCa}_2\}$ core. The assignment of absorption bands in the IR spectra was carried out in accordance with the data from literature [22,37] (Table 2).

The absorption band at 3609 cm^{-1} correspond to the $\nu(\text{OH})$ vibrations of coordinated methanol molecules and the bands around 3062 and 1248 cm^{-1} are assigned respectively to the stretching frequencies of phenolic $\nu(\text{OH})$ and phenolic $\nu(\text{C}-\text{OH})$. This confirms the presence of phenolic OH groups that do not participate in the coordination. The methyl groups of DMA molecules are characterized by valence oscillations $\nu(\text{CH})$ observed at 2934 cm^{-1} . The presence of $\nu(\text{C}=\text{O})$ valence oscillations at 1618 cm^{-1} of DMA molecules in the inner sphere indicates the participation of the carbonyl group in the coordination to calcium ions.

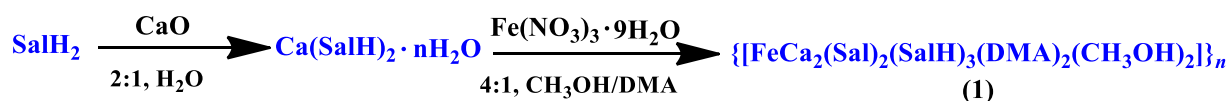
According to the data summarized in Table 1, in the case of coordination compound **1** the absorption band $\nu(\text{C}=\text{O})$ at 1655 cm^{-1} characteristic for the carboxylic group vibrations of the protonated acid are no longer present in the spectrum, instead two bands characteristic for $\nu_{\text{as}}(\text{COO}^-)$ at $1599 - 1511\text{ cm}^{-1}$ and $\nu_{\text{s}}(\text{COO}^-)$ at $1398 - 1374\text{ cm}^{-1}$ appear [37]. The difference $\Delta = [\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)]$ is approximately 201 and 137 cm^{-1} , which suggests that the salicylate anions coordinate in different coordination modes [22,37]. The bands at 1484 cm^{-1} and 1458 cm^{-1} correspond to $\nu(\text{C}=\text{C})(\text{aromatic})$ vibrations and the band located at 1325 cm^{-1} is due to the $\delta(\text{OH})(\text{phenolic})$ deformation vibrations. In the IR spectrum of compound **1**, there are absorption bands in the region $600 - 434\text{ cm}^{-1}$, which can be attributed to the $\nu(\text{FeO})$, $\nu(\text{CaO})$ valence vibrations [37].

Table 2

Absorption bands (cm^{-1}) in the IR spectra of salicylic acid (H_2Sal) and coordination compound **1.**

H_2Sal	1	Assignment
	3609 sh	$\nu(\text{OH})(\text{CH}_3\text{OH})$
3232 sh	3062 w	$\nu(\text{OH})(\text{phenolic})$
-	2934 vw	$\nu(\text{CH})(\text{DMA})$
1655 s	-	$\nu(\text{C}=\text{O})(\text{salicylic})$
-	1618 sh	$\nu(\text{C}=\text{O})(\text{DMA})$
1579 sh	1599 s	$\nu_{\text{as}}(\text{COO}^-)$
1528 sh	1511 m	
1482 sh	1484 sh	$\nu(\text{C}=\text{C})(\text{aromatic ring})$
1442 vs	1458 vs	
1384 w	1398 sh	$\nu_{\text{s}}(\text{COO}^-)$
	1374 m	
1324 w	1325 w	$\delta(\text{OH})(\text{phenolic})$
1243 s	1248 s	$\nu(\text{C}-\text{OH})(\text{phenolic})$
1188 sh	1192 vw	$\delta(\text{C}-\text{H})$
1154 s	1145 s	
1030 m	1031 s	
965 w	967 w	$\gamma(\text{CH})$
888 s	863 m	
784 s	760 vs	$\delta(\text{CH})(\text{outside the plan})$
757 vs	703 s	
693 vs		$\delta(\text{OCO})$
658 m	666 s	
-	600 w	$\nu_{\text{as}}(\text{MO})$
	581 w	
	536 m	
-	461 w	$\nu_{\text{s}}(\text{MO})$
	434 m	

where, M= Fe(III), Ca(II); vs- very strong; s- strong; m- medium; w- weak; vw- very weak, sh- shoulder.



Scheme 1. The synthesis of heteronuclear compound **1**.

Single crystal X-ray diffraction analysis and crystal structure description

Single crystal X-ray study has revealed that compound **1** represents an 1D coordination polymer with the composition $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$. The asymmetric part of the unit cell (Figure 1) comprises one Fe(III) and two Ca(II) atoms, five molecules of salicylic acid as two doubly deprotonated (Sal^{2-}) and three monodeprotonated (SalH^-), and molecules of DMA and CH_3OH involved in the coordination as neutral ligand. Selected interatomic distances and bond angles are presented in Table 3.

The Fe1 atom is coordinated by six oxygen atoms in a slightly distorted octahedral geometry whereas, Ca1 and Ca2 atoms are surrounded by eight and seven oxygen atoms, respectively, provided by coordinated methanol and dimethylacetamide molecules.

As shown in Figure 2, salicylate anions exhibit three different coordination functions. Thus, two monodeprotonated salicylate anions are coordinated in a bidentate bridging mode (Figures 2(a) and 2(b)) and one monodeprotonated salicylate anion which behaves as a tridentate-bridging ligand (Figure 2(c)). Two remaining double-deprotonated Sal^{2-} ligands act as pentadentate-bridging ligands (Figures 2(d) and 2(e)).

In the crystal, the asymmetric unit is auto-assembled over the centre of symmetry to generate one-dimensional coordination polymer running along *a* crystallographic axis, as shown in Figure 3. Thus, the salicylic anions bind the metal centres forming a 1D coordination polymer anchored with methanol and dimethylacetamide molecules. The non-coordinated hydroxyl groups of salicylic acid are involved in hydrogen bonding towards carboxylate oxygen atoms as acceptors of protons (Table 4).

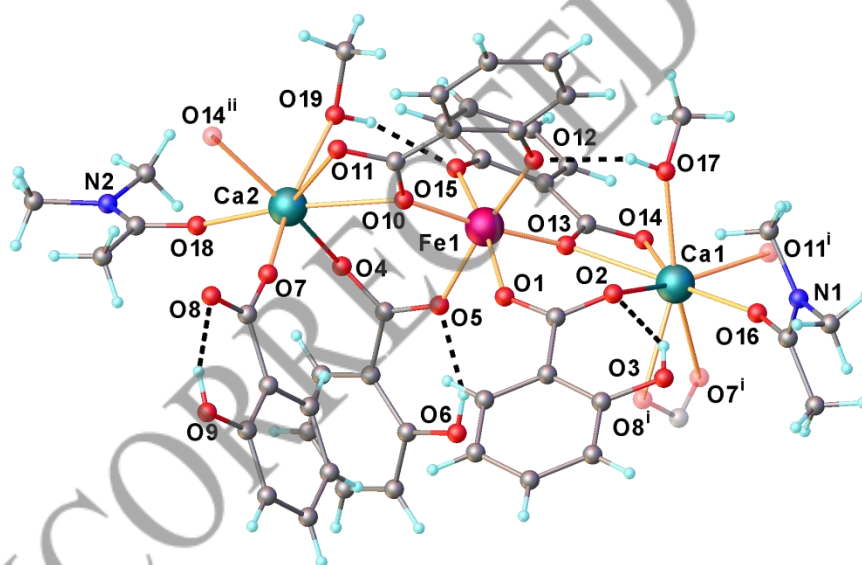


Figure 1. View of the asymmetric unit showing the coordination environment of the metal atoms for **1**. Only one position of disordered moieties is shown for clarity. Symmetry codes: ⁱ -1+x,+y,+z; ⁱⁱ 1+x,+y,+z.

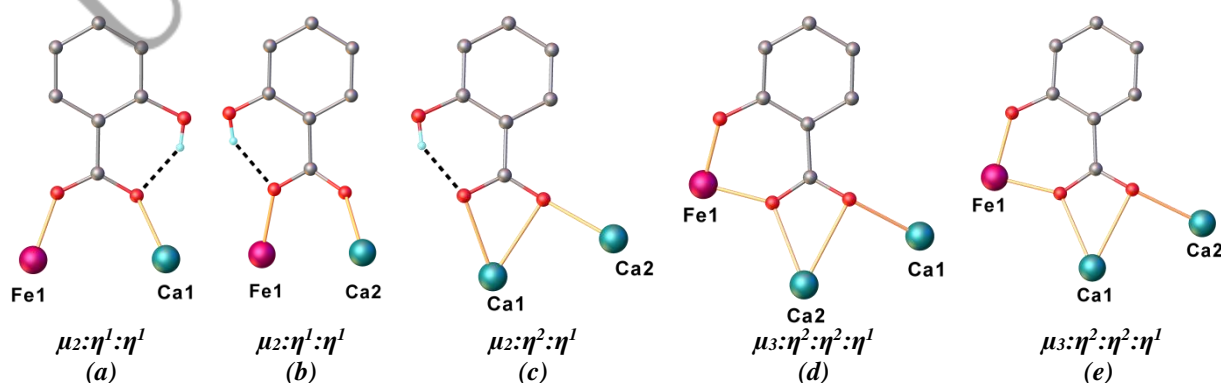


Figure 2. The coordination modes of the salicylic ligand in $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$.

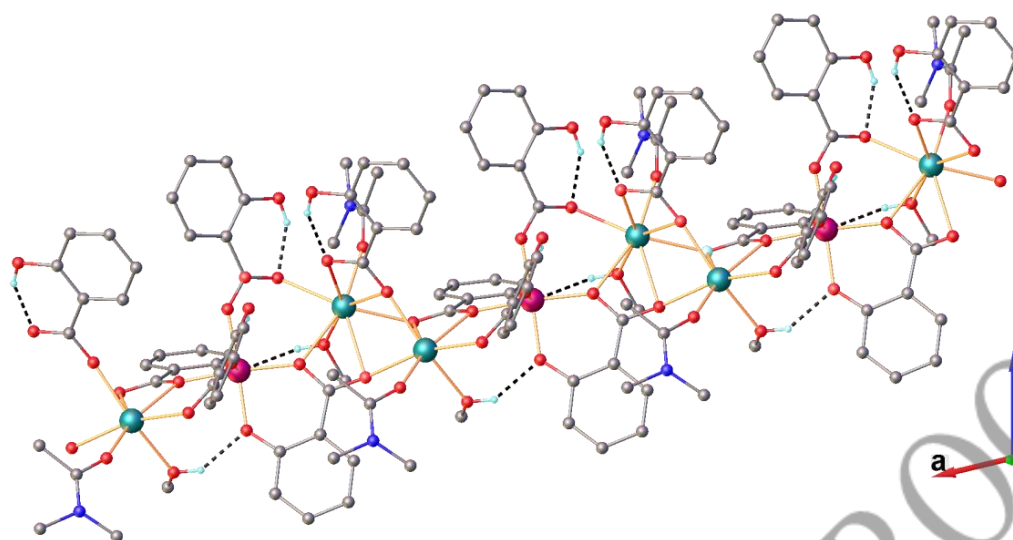


Figure 3. Fragment of the crystal structure of the coordination polymer $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$.

Table 3

Selected bond lengths [Å] and angles [°] for 1.

Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)
Fe1–O1	2.016(3)	Ca1–O7 ⁱ	2.571(7)	Ca2–O4	2.280(3)
Fe1–O5	2.030(3)	Ca1–O8 ⁱ	2.430(4)	Ca2–O7	2.256(6)
Fe1–O10	1.989(2)	Ca1–O11 ⁱ	2.351(2)	Ca2–O10	2.488(2)
Fe1–O12	1.967(3)	Ca1–O13	2.488(2)	Ca2–O11	2.674(3)
Fe1–O13	1.999(2)	Ca1–O14	2.583(2)	Ca2–O14 ⁱ	2.360(2)
Fe1–O15	1.964(2)	Ca1–O17	2.389(3)	Ca2–O18	2.288(3)
Ca1–O2	2.383(3)	Ca1–O16	2.295(3)	Ca2–O19	2.393(3)
Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
O1–Fe1–O5	80.6(1)	O12–Fe1–O13	89.3(1)	O15–Fe1–O13	87.6(9)
O10–Fe1–O1	91.0(1)	O13–Fe1–O1	93.9(1)	Ca2–O7–Ca1 ⁱ	95.6(2)
O10–Fe1–O5	93.4(1)	O13–Fe1–O5	89.8(10)	Ca1 ⁱ –O11–Ca2	90.7(8)
O10–Fe1–O13	174.6(1)	O15–Fe1–O1	171.8(1)	Fe1–O10–Ca2	126.6(1)
O12–Fe1–O1	91.1(1)	O15–Fe1–O5	91.3(1)	Fe1–O13–Ca1	127.9(1)
O12–Fe1–O5	171.6(1)	O15–Fe1–O10	88.0(9)		
O12–Fe1–O10	88.2(1)	O15–Fe1–O12	97.0(1)		

Symmetry transformations used to generate equivalent atoms: ⁱ 1+x,+y,+z.

Table 4

Hydrogen bond distances [Å] and angles [°] for 1.

<i>D</i> – <i>H</i> ··· <i>A</i>	<i>d</i> (<i>D</i> – <i>H</i>)	<i>d</i> (<i>H</i> ··· <i>A</i>)	<i>d</i> (<i>D</i> ··· <i>A</i>)	(DHA)
O17–H···O12	0.9(1)	2.0(2)	2.7(3)	145(3)
O19–H···O15	0.9(1)	2.0(3)	2.7(3)	143(3)
C37–H···O3	1.0	2.6	3.3(7)	126.4

Conclusions

By interaction between calcium salicylate and iron(III) nitrate in CH₃OH/DMA solvent mixture was obtained a new μ -oxo heteronuclear {FeCa₂}_n coordination polymer of salicylic acid which contains one iron(III) ion and two calcium(II) ions.

The structure of the $\{[\text{FeCa}_2(\text{Sal})_2(\text{SalH})_3(\text{DMA})_2(\text{CH}_3\text{OH})_2]\}_n$

coordination polymer was determined by X-ray diffraction analysis and confirmed by elemental analysis and IR spectroscopy. The infrared spectrum is in good agreement with structural information, which confirms that the salicylate anions coordinate in various modes, as a mono- and bideprotonated ligand, as well as the presence of methanol and dimethylacetamide molecules in the compound. The carboxyl group of the salicylic anions joins the metal centres into a one-dimensional coordination polymer in both chelating and bridging modes.

The coordination number of iron ion is six, being provided by oxygen atoms from carboxyl and hydroxyl groups, whilst for calcium ions the coordination number is 7 and 8, respectively, being

provided by the oxygen atoms from carboxylic groups, methanol and dimethylacetamide solvent molecules.

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