

# THE SYNTHESIS AND STUDY OF TETRANUCLEAR CLUSTER [Fe<sub>4</sub>O<sub>2</sub>(CCl<sub>3</sub>COO)<sub>8</sub>(THF)<sub>2</sub>(DMF)(H<sub>2</sub>O)]·THF

Denis Prodius<sup>a</sup>, Valeriu Mereacre<sup>a</sup>, Sergiu Shova<sup>b</sup>, Maria Gdaniec<sup>c</sup>, Yurii Simonov<sup>d</sup>,  
Lorenzo Sorace<sup>e</sup>, Andrea Caneschi<sup>e</sup>, Nicolae Stanica<sup>f</sup>, Ion Geru<sup>g</sup>, Constantin Turta<sup>\*a</sup>

<sup>a</sup>Institute of Chemistry of the Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova

<sup>b</sup>State University of Moldova, MD-2009 Chisinau, Moldova

<sup>c</sup>Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780, Poznań, Poland

<sup>d</sup>Institute of Applied Physics of the Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova

<sup>e</sup>Department of Chemistry and INSTM Research Unit, University of Florence, Florence, Italy

<sup>f</sup>Institute of Physical Chemistry "Murgulescu", Romanian Academy, Bucharest, Romania

<sup>g</sup>The Metrology and Material Analysis Centre, Academy of Sciences of Moldova, Chisinau, Moldova

\*Corresponding author: Fax:(37322) 739954; Tel:(37322) 739755; E-mail: turtalcba@yahoo.com; cturta@cc.acad.md

**Abstract:** The novel bis( $\mu_3$ -oxo) tetranuclear trichloroacetate cluster, [Fe<sub>4</sub>O<sub>2</sub>(CCl<sub>3</sub>COO)<sub>8</sub>(THF)<sub>2</sub>(DMF)(H<sub>2</sub>O)]·THF (**1**), has been synthesised and subsequently characterised by X-ray structure analysis, magnetic measurements and infra red (IR). The structure of cluster is "butterfly" type. The Fe···Fe separation has the value of 2.883(1) - 3.441(7) Å. The coordination number of iron (III) is 6. Magnetic studies reveal the presence of an antiferromagnetic exchange in the parallelogram skeletons of the tetranuclear species. Using the spin Hamiltonian  $H = -2J_{wb}(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_1) - 2J_{bb}\hat{S}_2\hat{S}_4 + g\mu_B(\hat{S}_{1z} + \hat{S}_{2z} + \hat{S}_{3z} + \hat{S}_{4z})B$ , the fitting parameters  $J_{bb} = -14.3 \text{ cm}^{-1}$ ,  $J_{wb} = -32.1 \text{ cm}^{-1}$ ,  $g = 2.07$ ,  $\rho_{\text{param.}} = 4.2 \%$ ,  $\theta_{\text{Curie-Weiss const.}} = -0.5 \text{ K}$  and  $R = 6.8 \cdot 10^{-5}$  were obtained.

**Keywords:** {Fe<sub>4</sub>O<sub>2</sub>} core; Homotetranuclear carboxylate; Crystal structure; Antiferromagnetic exchange.

## 1. Introduction

For a long time the permanent interest of the investigators to oxo- carboxylate complexes of transition metals was due to their usefulness in resolving the problems of theory of magnetism of coordination compounds [1-5] and practical problems connected with the specific catalysis [6] and biological active substances [7].

In the last few years this class of substances has become the focus of much attention by the development of the new scientific direction concerning the best way to obtain single molecule magnet (SMM) [8-10]. At the same time the oxo iron carboxylate complexes are good model compounds for the active centers of a number of metalloproteins such as: hemerythrin (Hr) [11, 12], ribonucleotide reductase (RR) [11, 12], purple acid phosphatases (PAPs) [11-14]; ferreascidin (Fasc) [15, 16], and ferritin (Fn) [17,18]. Hr, RR, PAPs contain dinuclear iron sites, Fasc – supposedly - three nuclear sites, and Fn – a large polynuclear iron oxide core. After the first publication of the synthesis and study the tetranuclear iron(III) trifluoroacetate [19-21] the large number of complexes of this series was synthesized and investigated by different methods [22-26].

In attempt to continue the previous studying and obtaining the model of the active centers of polyiron enzymes we report herein the synthesis of tetranuclear iron(III) complex with trichloroacetic acid.

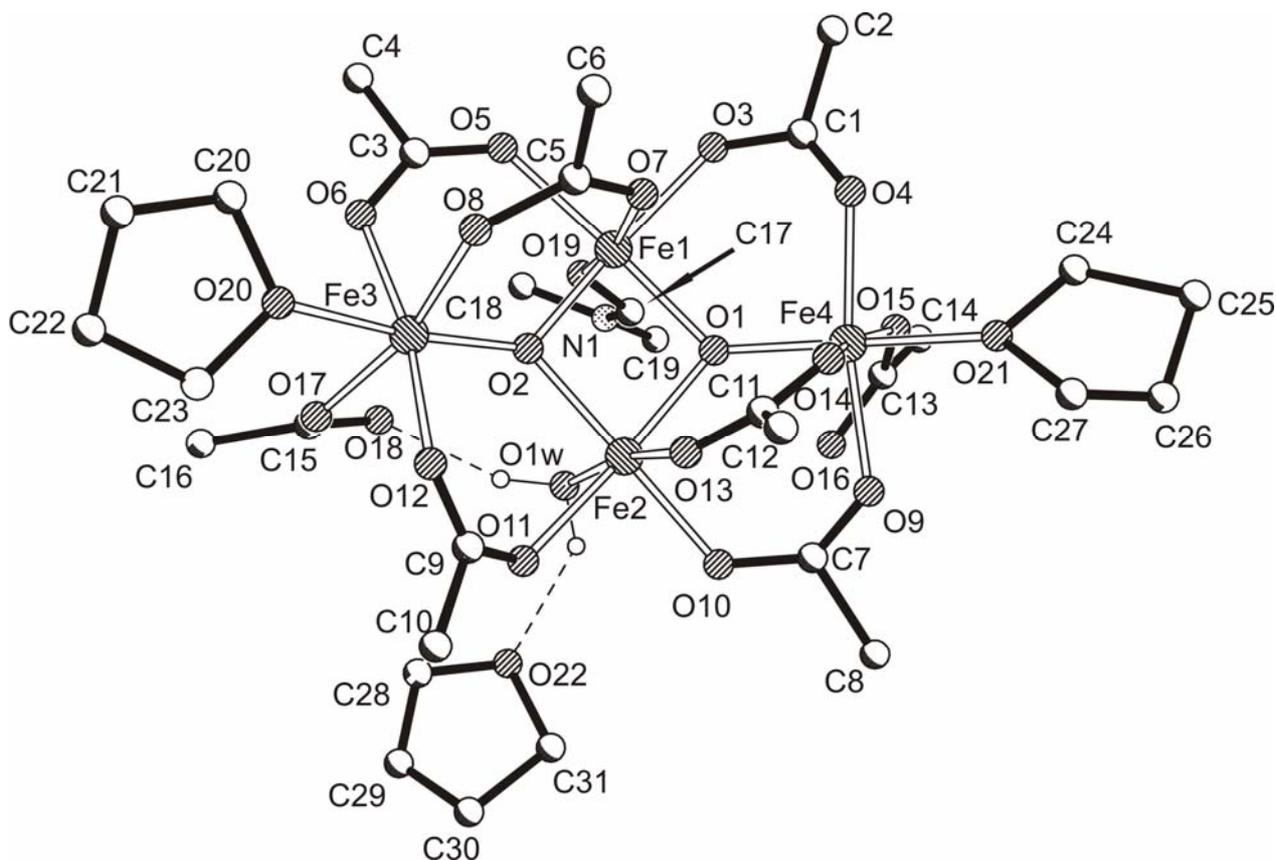
## 2. Results and discussion

Up to date various polynuclear complexes with chloro containing acetic acids have been synthesized and structurally characterized [27–31]. Most of these complexes were synthesized through step concerning treatment of basic acetates of d - elements with corresponding acids in aqueous solutions. It is worth mentioning that complex **1** was prepared by the procedure concerning the extract of the barium ion in heterotrinnuclear complex by sulphate anion in "water-THF-toluene" mixture.

### 2.1. Structure

The crystal **1** has a molecular structure build from neutral tetranuclear [Fe<sub>4</sub>O<sub>2</sub>(CCl<sub>3</sub>COO)<sub>8</sub>(THF)<sub>2</sub>(DMF)(H<sub>2</sub>O)] complexes and THF solvate molecules in 1:1 ratio. The X-ray study revealed that tetranuclear entity could be described as a typical "butterfly" type structure, as depicted in figure 1. The four metal atoms are linked through two  $\mu_3$ -oxo centers and six bidentate-bridged carboxylate ligands coordinated in *syn-syn* fashion. Other two carboxylate anions behave as monodentate ligands being coordinated to Fe(3) and Fe(4) atoms. The Fe···Fe separation within the Fe<sub>4</sub>( $\mu_3$ -O)<sub>2</sub> core exhibit the following values: Fe(1)-Fe(4) 3.441(7); Fe(1)-Fe(3) 3.372(6); Fe(1)-Fe(2) 2.883(5); Fe(2)-Fe(4) 3.373(7); Fe(2)-Fe(3) 3.437(6) Å (Tabl.2). In contrast to Fe(3) and Fe(4), Fe(1) and Fe(2) atoms coordinate as a monodentate ligand one DMF molecule (Fe(1)-O(19) = 2.03(2) Å) and one water molecule (Fe(2)-O(1w) = 2.02(2) Å), respectively. The coordinated water molecule O(1w) forms two H-bonds, one with the oxygen atoms of solvate THF and another with the monodentate carboxylate ligands with the distances O(1w)···O(18) 2.81(4), O(1w)H···O(18) 1.97, O(1w)···O(22) 2.74(3), O(1w)H···O(18) 1.99 (Å) and angles O(1w)HO(18) 155.1, O(1w)HO(22) 140.2 (°). The Fe<sub>4</sub>( $\mu_3$ -O)<sub>2</sub> core is essentially non-planar. The dihedral angle between two Fe<sub>3</sub>( $\mu_3$ -O) fragments is equal to 33.0(1)°. The deviation of  $\mu_3$ -oxigen atoms from the respective plane is different: 0.35(1) Å for O(1) and 0.24(2) Å for O(2). Each iron ions has an O<sub>6</sub> slightly distorted octahedron coordination, but their environment is different. In particular, the

coordination site of the Fe(3) and Fe(4), which comprises only one  $\mu_3$ -O bridging atom, are similar and differ from that for Fe(1) and Fe(2) atoms, which include only two  $\mu_3$ -O bridging atoms (Fig. 1).



**Figure 1.** View of the unsymmetrical unit in crystal structure of  $[\text{Fe}_4\text{O}_2(\text{CCl}_3\text{COO})_8(\text{THF})_2(\text{DMF})(\text{H}_2\text{O})]\cdot\text{THF}$  (1). The chloride atoms and the H atoms bonded to carbon are omitted for clarity.

At the same time, the coordination site of the last pair is also different as the coordination of Fe(1) atoms is completed by DMF molecule (Fe(1)–O(19) = 2.03(2) Å), while the coordination of Fe(2) – by one water molecule (Fe(2)–O(1w) = 2.02(2) Å).

**Table 1.** Selected bond lengths (Å) and angles (deg) for  $[\text{Fe}_4\text{O}_2(\text{CCl}_3\text{COO})_8(\text{THF})_2(\text{DMF})(\text{H}_2\text{O})]\cdot\text{THF}$ .

O(1)–Fe(1)	1.942(18)	O(1)–Fe(2)	1.978(17)
O(2)–Fe(3)	1.85(2)	O(2)–Fe(1)	1.882(18)
O(2)–Fe(2)	1.946(19)	O(1w)–Fe(2)	2.01(2)
O(3)–Fe(1)	1.954(18)	O(4)–Fe(4)	2.05(2)
O(5)–Fe(1)	2.02(2)	O(1)–Fe(4)	1.85(2)
O(7)–Fe(1)	2.05(2)	O(6)–Fe(3)	2.074(16)
O(9)–Fe(4)	2.04(2)	O(8)–Fe(3)	2.03(2)
O(11)–Fe(2)	2.09(2)	O(10)–Fe(2)	2.03(2)
O(13)–Fe(2)	2.084(19)	O(12)–Fe(3)	2.073(15)
O(15)–Fe(4)	1.946(18)	O(14)–Fe(4)	2.051(19)
O(19)–Fe(1)	2.03(2)	O(17)–Fe(3)	2.00(2)
O(21)–Fe(4)	2.09(3)	O(20)–Fe(3)	2.091(18)
C(1)–O(4)	1.295(19)	C(1)–O(3)	1.298(19)
C(1)–C(2)	1.54(4)	C(3)–O(5)	1.14(4)
C(3)–O(6)	1.42(3)	C(3)–C(4)	1.53(5)
C(5)–O(7)	1.40(2)	C(5)–O(8)	1.41(2)
C(5)–C(6)	1.34(4)	C(7)–O(9)	1.25(2)
C(7)–O(10)	1.25(2)	C(7)–C(8)	1.64(4)
C(9)–O(11)	1.257(16)	C(9)–O(12)	1.257(16)
C(11)–O(14)	1.209(18)	C(9)–C(10)	1.53(3)

C(11)-C(12)	1.56(4)	C(11)-O(13)	1.209(18)
C(13)-O(16)	1.28(5)	C(13)-O(15)	1.20(4)
C(15)-O(17)	1.27(4)	C(13)-C(14)	1.53(4)
C(15)-C(16)	1.64(6)	C(15)-O(18)	1.32(4)
C(17)-N(1)	1.366(19)	C(17)-O(19)	1.25(4)
C(18)-N(1)	1.38(6)	C(19)-N(1)	1.42(4)
C(20)-O(20)	1.45(2)	C(20)-C(21)	1.48(2)
C(21)-C(22)	1.48(2)	C(22)-C(23)	1.48(2)
C(23)-O(20)	1.45(2)	C(24)-O(21)	1.45(2)
C(24)-C(25)	1.48(2)	C(25)-C(26)	1.48(2)
C(26)-C(27)	1.48(2)	C(27)-O(21)	1.45(2)
C(28)-O(22)	1.45(2)	C(28)-C(29)	1.47(2)
C(29)-C(30)	1.48(2)	C(30)-C(31)	1.48(2)
C(31)-O(22)	1.45(2)		

O(2)-Fe(1)-O(1)	84.7(8)	O(2)-Fe(1)-O(19)	96.4(9)
O(1)-Fe(1)-O(19)	94.3(8)	O(2)-Fe(1)-O(3)	174.1(9)
O(1)-Fe(1)-O(3)	95.0(9)	O(19)-Fe(1)-O(3)	89.5(8)
O(2)-Fe(1)-O(5)	95.2(9)	O(1)-Fe(1)-O(5)	177.9(8)
O(19)-Fe(1)-O(5)	83.7(9)	O(3)-Fe(1)-O(5)	85.2(9)
O(2)-Fe(1)-O(7)	90.3(8)	O(1)-Fe(1)-O(7)	94.5(7)
O(19)-Fe(1)-O(7)	169.4(7)	O(3)-Fe(1)-O(7)	83.8(8)
O(5)-Fe(1)-O(7)	87.6(8)	O(2)-Fe(1)-Fe(2)	41.9(6)
O(1)-Fe(1)-Fe(2)	43.1(5)	O(19)-Fe(1)-Fe(2)	93.7(5)
O(3)-Fe(1)-Fe(2)	138.0(7)	O(5)-Fe(1)-Fe(2)	136.7(7)
O(7)-Fe(1)-Fe(2)	96.8(5)	O(2)-Fe(2)-O(1)	82.2(8)
O(2)-Fe(2)-O(1W)	88.2(9)	O(1)-Fe(2)-O(1W)	101.1(7)
O(2)-Fe(2)-O(10)	170.4(8)	O(1)-Fe(2)-O(10)	94.8(8)
O(1W)-Fe(2)-O(10)	83.3(9)	O(2)-Fe(2)-O(13)	98.5(8)
O(1)-Fe(2)-O(13)	88.1(7)	O(1W)-Fe(2)-O(13)	169.3(7)
O(10)-Fe(2)-O(13)	90.5(8)	O(2)-Fe(2)-O(11)	93.1(8)
O(1)-Fe(2)-O(11)	169.3(8)	O(1W)-Fe(2)-O(11)	88.3(8)
O(10)-Fe(2)-O(11)	91.3(8)	O(13)-Fe(2)-O(11)	83.1(8)
O(2)-Fe(2)-Fe(1)	40.3(6)	O(1)-Fe(2)-Fe(1)	42.1(5)
O(1W)-Fe(2)-Fe(1)	92.7(5)	O(13)-Fe(2)-Fe(1)	97.9(4)
O(10)-Fe(2)-Fe(1)	135.3(6)	O(11)-Fe(2)-Fe(1))	133.2(6)
O(2)-Fe(3)-O(17)	101.4(9)	O(2)-Fe(3)-O(8)	90.1(9)
O(17)-Fe(3)-O(8)	167.0(9)	O(2)-Fe(3)-O(6)	94.4(7)
O(17)-Fe(3)-O(6)	85.4(7)	O(8)-Fe(3)-O(6)	87.7(7)
O(2)-Fe(3)-O(12)	97.0(7)	O(17)-Fe(3)-O(12)	89.4(7)
O(8)-Fe(3)-O(12)	95.3(7)	O(6)-Fe(3)-O(12)	168.2(8)
O(2)-Fe(3)-O(20)	171.3(9)	O(17)-Fe(3)-O(20)	87.3(8)
O(8)-Fe(3)-O(20)	81.2(8)	O(6)-Fe(3)-O(20)	85.2(7)
O(12)-Fe(3)-O(20)	84.0(7)	O(1)-Fe(4)-O(15)	99.4(9)
O(1)-Fe(4)-O(9)	95.3(9)	O(15)-Fe(4)-O(9)	91.7(9)
O(1)-Fe(4)-O(4)	94.5(9)	O(15)-Fe(4)-O(4)	88.3(9)
O(9)-Fe(4)-O(4)	170.1(11)	O(1)-Fe(4)-O(14)	93.5(9)
O(15)-Fe(4)-O(14)	167.1(12)	O(9)-Fe(4)-O(14)	86.8(8)
O(4)-Fe(4)-O(14)	91.1(8)	O(1)-Fe(4)-O(21)	175.6(8)
O(15)-Fe(4)-O(21)	85.0(10)	O(9)-Fe(4)-O(21)	85.0(10)
O(4)-Fe(4)-O(21)	85.1(9)	O(14)-Fe(4)-O(21)	82.1(10)

## 2.2. Infrared spectra

The solid state IR spectra of **1** indicate the presence of carboxylate, THF, H<sub>2</sub>O and {Fe<sub>4</sub>O<sub>2</sub>} groups. The characteristic vibration frequencies for THF groups appear at ~3450-3600 and 2800–3000 cm<sup>-1</sup>. At the same time it is possible to appreciate the presence of a double pair of carboxylate stretching vibrations  $\nu_{as}$  (COO) and  $\nu_s$  (COO) at 1645 and 1670 cm<sup>-1</sup>, and 1380 cm<sup>-1</sup> respectively i.e. two types of carboxylate group in their crystal structures are present which is in accordance with X-ray data. These bands are shifted to lower energy by 45–75 cm<sup>-1</sup> relative to the trinuclear basic acetates [32] due to the replacement of the CH<sub>3</sub> radical by the much more powerfully electron-accepting CCl<sub>3</sub>

moieties which weaken the M - O<sub>carb</sub> force constant. The  $\nu_{as}$  (C-Cl) (A'', A') vibration frequencies for CCl<sub>3</sub> groups are present at 832 (s) and 826 (s) cm<sup>-1</sup> [33].

### 2.3. Magnetic properties

The magnetic properties of compound **1** have been measured in the 300 – 1.8 K range of temperature. At 300 K the value of  $\chi_M \cdot T$  is 3.91 cm<sup>3</sup>·K·mol<sup>-1</sup>. Lowering the temperature this value is diminished gradually and at 1.8 K is equal 0.10 cm<sup>3</sup>·K·mol<sup>-1</sup> thus indicating on antiferromagnetic interaction between ions of iron (III). In order to describe the magnetic properties of the investigated complex with the geometry, which is presented in scheme 1, the spin Hamiltonian (equation 1) model was used [4, 5].

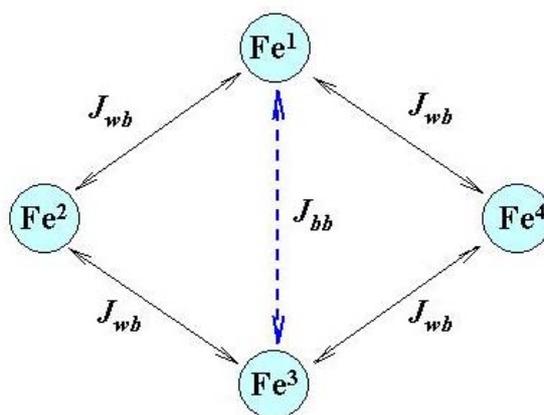
$$\hat{H}_{total} = \hat{H}_z + \hat{H}_{HDvV}, \quad (1)$$

where the isotropic (Heisenberg) exchange coupling term is described by

$$\hat{H}_{HDvV} = -2J_{wb}(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_1) - 2J_{bb}\hat{S}_2\hat{S}_4 \quad (2)$$

and Zeeman interaction of the Fe(III) spins with the applied magnetic field B, assumed in the z direction, is given by

$$\hat{H}_z = g\mu_B(\hat{S}_{1z} + \hat{S}_{2z} + \hat{S}_{3z} + \hat{S}_{4z}) \quad (3)$$



Scheme 1.

where  $\hat{S}_i$  is the spin operator on the  $i_{th}$  Fe(III) ion;  $J$  is the exchange integral couplings Fe(III) ions; (The sign of  $J$  is positive for parallel and negative for antiparallel spin coupling);  $g$  is the electronic gyromagnetic ratio;  $\mu_B$  is the Bohr magneton and B – magnetic field strength.

The original least-squares fitting computer program FDHM [34] with a Full Diagonalisation of Hamiltonian Matrix approach was employed to fit  $(\chi T)_{exp}$  vs. T, in order to obtain the exchange couplings constants. By use of the

spin product basis set of spin wave functions  $\psi = |m_{S_1} m_{S_2} m_{S_3} m_{S_4}\rangle$  a total of 1296 ( $= \prod_{i=1}^4 (2S_i + 1)$ ) spin wave

functions are obtained. The action of the spin Hamiltonian (1) on these wave function yields energy levels distributed with coupled spin quantum numbers,  $0 \leq S_t \leq 10$ .

The energy levels were determined by diagonalising the matrix

$$H_{ij} (H_{ij} = \langle \psi_i | \hat{H}_{total} | \psi_j \rangle) \quad (4)$$

The diagonalisation was simplified by block-factoring the matrix into  $M_{S_i}$  ( $= \sum_{i=1}^4 m_{S_i}$ ) submatrices, with the corresponding dimensions 1, 4, 10, 20, 35, 56, 80, 104, 125, 140, 146.

The magnetic susceptibilities of the compound were calculated from the spin-coupled wave function by using a simplified form of the Van Vleck equation [2]

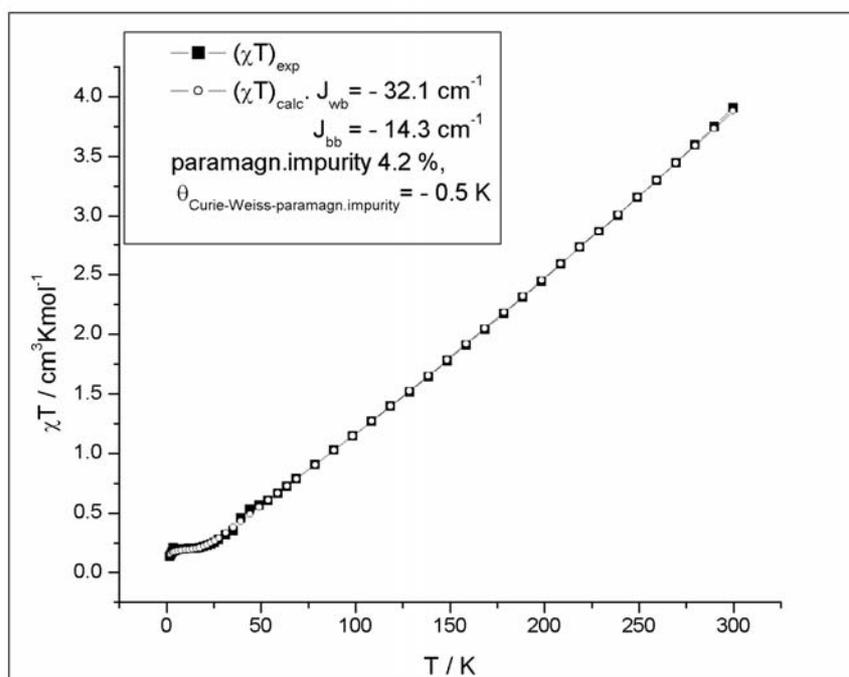
$$\chi_{mol} = \frac{N_A}{kT} \frac{\sum_{i=1,n} |\langle \psi_i | \hat{\mu} | \psi_i \rangle|^2 \exp(-E_i / kT)}{\sum_{i=1,n} \exp(-E_i / kT)} \quad (5)$$

$$\chi_{mol} = (1 - \rho) \frac{N_A}{kT} \frac{\sum_{i=1,n} |\langle \psi_i | \hat{\mu} | \psi_i \rangle|^2 \exp(-E_i / kT)}{\sum_{i=1,n} \exp(-E_i / kT)} +$$

$$\rho \frac{1}{3} \frac{N_A \mu_B^2}{k} \bar{g}^{-2} \frac{S_{Fe(III)}(S_{Fe(III)} + 1)}{1 - \frac{\theta_{Curie-Weiss}}{T}}$$

where  $E_i$  is the energy level with wave function  $\psi_i$  and  $\hat{\mu}$  is the moment operator given by  $\hat{\mu} = g\mu_B \sum_{i=1,4} \hat{S}_i$ .

The results of a least-squares fit of the magnetic data are illustrated in Fig. 2 as plots of the  $(\chi T)_{obs.}$  and  $(\chi T)_{calc.}$  vs. T.



**Figure 2. Temperature dependence of the magnetic susceptibility ( $\chi T$  vs. T) of the 1 and best fit curve obtained with parameters reported in the text.**

The calculated curve drawn through the experimental points represents the best fit of the model using the fitted parameters:  $J_{wb} = -32.1 \text{ cm}^{-1}$ ,  $J_{bb} = -14.3 \text{ cm}^{-1}$ ,  $\bar{g} = 2.07$ ,  $\rho_{\text{par. imp.}} = 4.2 \%$ ,  $\theta_{\text{Curie-Weiss const.}} = -0.5 \text{ K}$ ,  $R = 6.8 \cdot 10^{-5}$ , where

$$R \equiv \frac{\sum [(\chi T)_{obs.} - (\chi T)_{calc.}]^2}{\sum (\chi T)_{obs.}^2}$$

- the reliability factor.

From the acquired data it is obvious that the absolute value of magnetic exchange parameter is very close to literature data [20, 22-26].

### 3. Conclusion

The novel bis( $\mu_3$ -oxo) tetranuclear trichloroacetate cluster,  $[\text{Fe}_4\text{O}_2(\text{CCl}_3\text{COO})_8(\text{THF})_2(\text{DMF})(\text{H}_2\text{O})] \cdot \text{THF}$  (**1**), has been synthesised and subsequently characterised by X-ray structure analysis, magnetic measurements and infra red (IR). The structure of cluster is “butterfly” type and is typical for such class of clusters. Magnetic studies reveal the presence of an antiferromagnetic exchange in the parallelogram skeletons of the tetranuclear species with next fitting parameters:  $J_{bb} = -14.3 \text{ cm}^{-1}$ ,  $J_{wb} = -32.1 \text{ cm}^{-1}$ ,  $\bar{g} = 2.07$ ,  $\rho_{\text{param. impur.}} = 4.2 \%$ ,  $\theta_{\text{Curie-Weiss const.}} = -0.5 \text{ K}$  and  $R = 6.8 \cdot 10^{-5}$ . It is necessary to mention that the antiferromagnetic interaction between Fe1 and F3 is unexpected but according [35] the

value and sign of this parameter doesn't have any importance in fitting process of experimental and theoretical data. This fact needs the new conception in interpretation.

#### 4. Experimental

*General:* The carbon and hydrogen content of complex was determined by standard micro-methods in the group of microanalysis of the Institute of Chemistry of the Academy of Sciences of Moldova.

IR spectrum of polycrystalline sample was recorded as vaseline mulls on a Specord M-75 spectrophotometer.

*Synthesis* of  $[\text{Fe}_4\text{O}_2(\text{CCl}_3\text{COO})_8(\text{THF})_2(\text{DMF})(\text{H}_2\text{O})]\cdot\text{THF}$  (**1**). The red tetrahydrofuran solution (THF, 20 mL) of  $[\text{Fe}_2\text{BaO}(\text{CCl}_3\text{COO})_6(\text{THF})_6]\cdot 0,5\text{H}_2\text{O}\cdot 0,5\text{THF}$  (2.15 g, 1.286 mmol) [36] and aqueous solution (20 mL) of  $\text{La}_2(\text{SO}_4)_3\cdot 9\text{H}_2\text{O}$  (0.62 g, 0.849 mmol) were added to toluene (40 mL) and the mixture stirred for 2 h after which "toluene-THF" orange layer was carefully removed out and kept at room temperature until all solvent was evaporated. The obtained orange powder was re-dissolved in DMF/THF/heptane (1:9:2) mixture (12 mL). After three days light orange single crystals of **1** grew that were suitable for X-ray analysis. Yield: 0.17 g (14 % based on Fe). Elemental analysis (%): Found: C, 20.86; H, 1.75; Fe, 12.12 %. Calcd. for  $(\text{C}_{31}\text{H}_{33}\text{Cl}_{24}\text{NO}_{23}\text{Fe}_4)$ : C, 20,00; H, 1.78; Fe, 12.00.

IR data show (vaseline mulls,  $\text{cm}^{-1}$ ): 3650m, 3470mb, 1700m, 1673msh, 1645s; 1593s; 1590m; 1380s, 1340s; 1010w; 940w; 748 sh; 720m; 675m; 670s; 469m; 440m.

*Magnetic measurements.* Variable temperature susceptibility of **1** was measured with an Oxford Instruments Vibrating Sample Magnetometer (VSM) working between 0 and 12 T and in the 1.8–300.0 K temperature range. The diamagnetic Pascal's constants were used to correct the magnetic values [4, 5].

*Crystallographic data.* X-ray diffraction experimental data for **1** were collected at 100 K on a Kuma KM4CCD diffractometer (monochromated  $\text{MoK}_\alpha$  radiation). The crystal was positioned at the distance of 70 mm from the CCD chamber. Reflections of 142 frames in one set were collected with  $\omega$  angle between the frames  $0.5^\circ$ . Intensity data were corrected for the Lorentz and polarization effects. The structure was solved by direct methods [37] and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for non-H atoms [38]. The  $\text{CH}_2$  hydrogen atoms of THF moieties were located on  $\Delta F$  map and their distances to C atoms have been standardized to 0.96 Å with the isotropic displacement parameters fixed at  $1.2 \times U_{\text{eq}}$  of the relevant carbon atom. Positional parameters of H-atoms of coordinated water molecules were verified by the geometric parameters of the corresponding hydrogen bonds. The structural parameters together with details of data collection and refinement for **1** are given in Table 2, while selected bond lengths and angles – in Table 1.

**Table 2. Summary of Crystal Data and refinement details for  $[\text{Fe}_4\text{O}_2(\text{CCl}_3\text{COO})_8(\text{THF})_2(\text{DMF})(\text{H}_2\text{O})]\cdot\text{THF}$  (**1**).**

Empirical formula	$\text{C}_{31}\text{H}_{33}\text{Cl}_{24}\text{Fe}_4\text{NO}_{23}$
$M$	1861.78
Wavelength, Å	0.71073
Crystal system, Space group	Monoclinic, $P2_1/n$
$a$ , Å	14.215(3)
$b$ , Å	37.018(7)
$c$ , Å	14.341(3)
$\beta$ , deg	109.11(3)
$V$ , Å <sup>3</sup>	7131(3)
$Z$	4
$\rho_{\text{(calcd.)}}$ , $\text{Mg/m}^3$	1.734
$\mu_{\text{Mo}}$ , $\text{mm}^{-1}$	1.760
Crystal size, mm	$0.3 \times 0.25 \times 0.20$
$\theta$ range, deg	3.43 to 23.26
Number of reflections:	
Measured	7374
Unique	5296 [ $R_{\text{int}} = 0.1012$ ]
Number of refined parameters	258
GOOF for $F^2$	1.042
$^aR$	0.1402
$^b_wR$	0.3865
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ , $\text{e}\text{Å}^3$	1.035 and -0.923

$^aR = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $^b_wR = [\sum w(|F_o|^2 - |F_c|^2|)^2 / \sum w|F_o|^2]^2]^{1/2}$

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