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Synthesis and Crystal Structure of $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4](NO_3)_8 \cdot 2H_2O$

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Abstract—Crystals of the tetranuclear complex $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4](NO_3)_8 \cdot 2H_2O$ are obtained by the slow evaporation of an aqueous solution of iron(III) nitrate and isonicotinic acid. According to the X-ray diffraction data, four metal atoms lie in the same plane and together with two μ_3-O oxygen atoms form the fragment $[Fe_4(\mu_3\text{-}O)_2]^{10+}$. The $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4]^{8+}$ cation has been obtained and structurally characterized for the first time.

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INTRODUCTION

Processes of hydrolysis of Fe(III) compounds are studied insufficiently because of their kinetic lability and high affinity to the formation of X-ray amorphous polynuclear or polymeric complexes. The study of the polynuclear iron(III) oxo/hydroxo-bridged complexes is aimed at creating new functional materials, first of all, those with interesting magnetic properties [1–9].

The present work is devoted to the synthesis of the new tetranuclear iron(III) compound $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4](NO_3)_8 \cdot 2H_2O$ (**I**) and to the study of its crystal structure.

EXPERIMENTAL

The reagents used were of reagent grade. The synthesis was carried out in air. Analyses for C, H, and N were conducted at the Microanalysis Laboratory of the Institute of Inorganic Chemistry (Karlsruhe, Germany). IR spectra were recorded on an IFS-28 Fourier spectrometer (Bruker) in the 4000–300 cm^{-1} interval (KBr pellets).

Synthesis of compound I. A solution of isonicotinic acid (0.06 g, 0.48 mmol) in a mixture of CH_3CN (1.2 ml), water (1.2 ml), and 1 M KOH (0.6 ml, 0.6 mmol) was added with stirring to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (0.61 g, 1.5 mmol) in water (3 ml). The solution color changed from orange to brown. The solution was stirred for 4 h and left to evaporate in air to a volume of 0.5 ml. Well cut red-brown crystals were formed, filtered off, and dried in air for a day. The yield was 0.050 g (27% based on isonicotinic acid).

Found (%):	C 19.29;	H 2.74;	N 11.13.
For $C_{24}H_{44}Fe_4N_{12}O_{46}$			
Anal. calcd. (%):	C 19.74;	H 3.04;	N 11.51.

IR, cm^{-1}: 3401, 3076, 2925, 2853, 1602, $\nu(NO_3^-)$, 1507, 1415 $\nu_s(COO^-)$ 1385 $\nu(NO_3^-)$, 1246, 1190, 1158, 1096, 1044, 1008, 825, 763, 682, 653, 599, 529, 466.

X-ray diffraction analysis. The unit cell parameters and the three-dimensional set of reflection intensities for structure **I** were obtained according to a standard procedure on a STOE IPDS II automated diffractometer (MoK_α radiation, graphite monochromator, CCD) using the SAINT program package [10]. An absorption correction was applied by intensities of equivalent reflections [10]. The structure was solved by a direct method and refined by the full-matrix least-squares method in the anisotropic (for non-hydrogen atoms) approximation (SHELX-97) [11]. Positions of the hydrogen atoms of isonicotinate were calculated geometrically and refined by the riding model. The hydrogen atoms of the aqua ligands and molecules of water of crystallization were not located. The crystallographic characteristics and details of diffraction experiment and crystal structure refinement are given in Table 1. Selected bond lengths and bond angles were deposited with the Cambridge Crystallographic Data Centre (no. 724 395; http://www.ccdc.cam.ac.uk/products/csd/request/) and are available from the authors.

RESULTS AND DISCUSSION

Compound **I** was obtained by the slow evaporation of an aqueous solution containing an excess of iron(III) nitrate, isonicotinic acid, and KOH.

Red-brown crystals are stable in air and insoluble in water, alcohol, and CH_3CN.

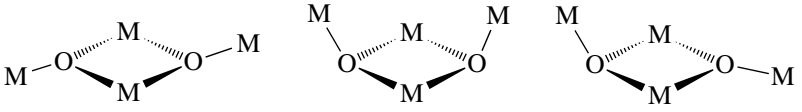
The IR spectrum of compound **I** in the region from 3700 to 3100 cm^{-1} exhibits a broad band of stretching vibrations of the water molecules. An analysis of published data [12, 13] and a comparison of the IR spectra of 4-pyridinecarboxylic acid with the spectra of the complexes made it possible to identify the absorption band of the carboxylate group of the isonicotinate ion coordinated to the metal atoms: the asymmetric vibrations appear at 1602 cm^{-1} and the symmetric vibrations are observed at 1415 cm^{-1}. The bands of vibrations of the nitrate anions are observed at 1385 cm^{-1}.

The structural units of the crystal of compound **I** are centrosymmetric tetranuclear cationic complexes $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4]^{8+}$ (Fig. 1), nitrate anions, and molecules of water of crystallization. Two crystallographically independent iron atoms have the octahedral environment. The Fe(1) atom is coordinated by three oxygen atoms of the aqua ligands (O(2M), O(3M), and O(4M)), two O atoms of two carboxylate groups of the μ_2,η^2-bridging isonicotinates (O(1) and O(3)), and the μ_3-bridging oxo ligand O(1M). The Fe(2) atom is coordinated by two oxygen atoms of the aqua ligands (O(5M) and O(6M)), two O atoms of two carboxylate groups of isonicotinates (O(2) and O(4)), and two μ_3-O atoms (O(1M)). The Fe–O distances (1.8439(19)–2.1559(19) Å, average 2.01(8) Å) are typical of the oxygen-containing iron(III) complexes [14–19]. Four Fe atoms lie in the same plane. The average deviation of the oxygen atoms of the carboxylate (O(1)–O(4)), oxo (O(1M)), and aqua ligands (O(4M)) from the Fe_4 plane is 0.07(5) Å, and two μ_3-bridging oxo ligands exhibit the maximum deviation (0.151 Å). For all atoms of the $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4]^{8+}$ cation lying in the Fe_4 plane, the average deviation from the plane is 0.14(12) Å. The isonicotinate ligands bind in pairs the iron atoms due to the coordination of the carboxy group according to the μ_2,η^2 mode and are arranged in the equatorial plane of the cationic complex. The distances between the Fe(1) and Fe(2) atoms are 3.424(3) and 3.445(2) Å, and the Fe(2)–Fe(2)^a distance ($-x + 1, -y, -z + 1$) is considerably shorter (2.9272(9) Å). The $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4]^{8+}$ cations in crystal are joined into parallel chains along the *y* axis due to hydrogen bonding between the O(3M) and O(4M) aqua ligands of the adjacent complexes (O···O 2.738 Å) (Fig. 2). The cation packing is presented in Fig. 3. The remaining space is filled with molecules of water of crystallization and nitrate anions.

Table 1. Crystallographic characteristics and details of the diffraction experiment and refinement of the crystal structure of compound **I**

Parameter	Value
FW	1460.11
Temperature, K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	10.154(3)
b, Å	25.032(6)
c, Å	10.687(3)
β, deg	106.46(2)
V, Å^3	2605.0(12)
Z	2
ρ_{calcd}, g/cm^3	1.861
μ, mm^{-1}	1.228
F(000)	1488
Crystal sizes, mm	0.40 × 0.30 × 0.25
θ range, deg	2.15–27.04
Index range	$-13 < h < 13, -33 < k < 31, -14 < l < 14$
N_{hkl} measured/N_{hkl} independent	20497/5511 (R_{int} = 0.0784)
N_{hkl} with $F > 4\sigma(F)$	5206
T_{max}/T_{min}	0.7488/0.6394
Number of refined parameters	389
GOOF for F^2	1.072
R factor for $F > 4\sigma(F)$	R_1 = 0.0407, wR_2 = 0.1156
R factor for all reflections	R_1 = 0.0430, wR_2 = 0.1240
Extinction coefficient	0.0143(13)
Residual electron density (max/min), *e* Å^{-3}	0.829/–0.647

The tetranuclear Fe(III) complexes containing the Fe_4O_2 fragment are known [14–19]. Such compounds containing the planar (A) or nonplanar (B, C) Fe_4O_2 fragment demonstrate interesting magnetic properties.



An important feature of the synthesized compound is the presence of four pyridinic nitrogen atoms lying in one plane, which provides possibilities of synthesis of organometallic coordination polymers from compound **I**.

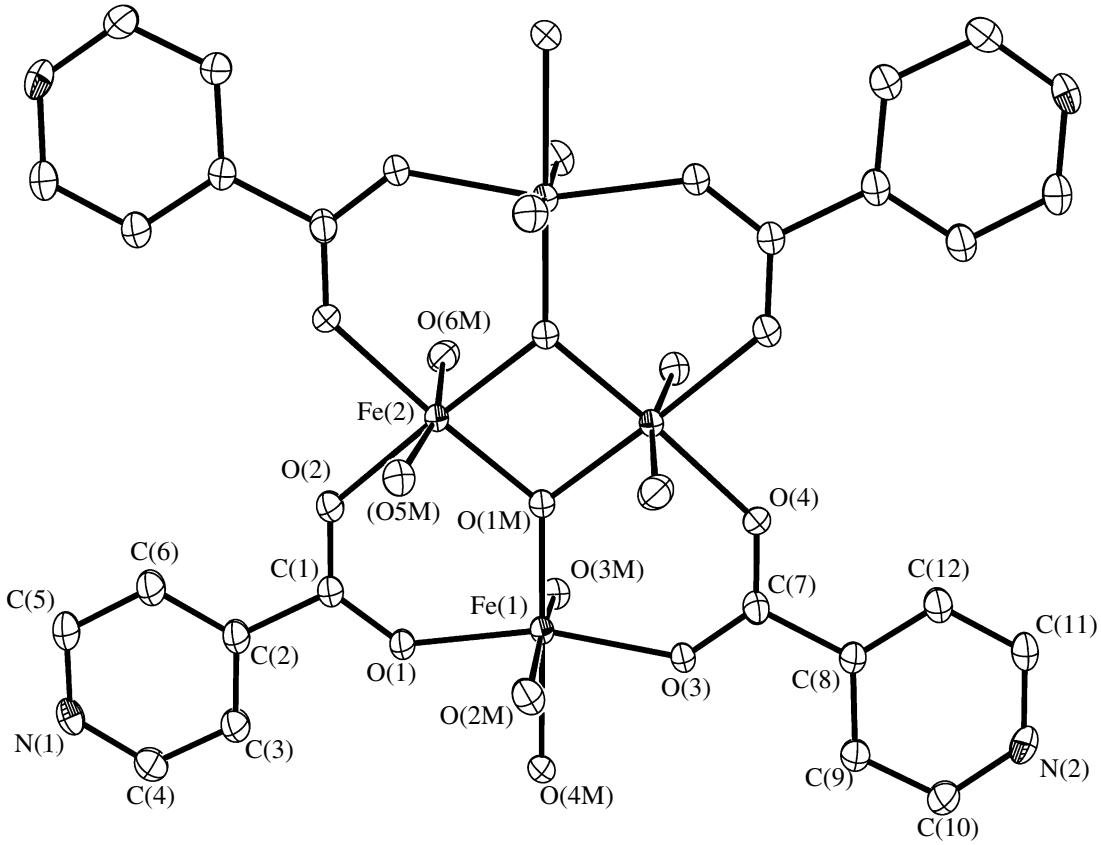


Fig. 1. Coordination environment of the iron atoms in the $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4]^{8+}$ tetranuclear complex in structure **I**. Hydrogen atoms are omitted.

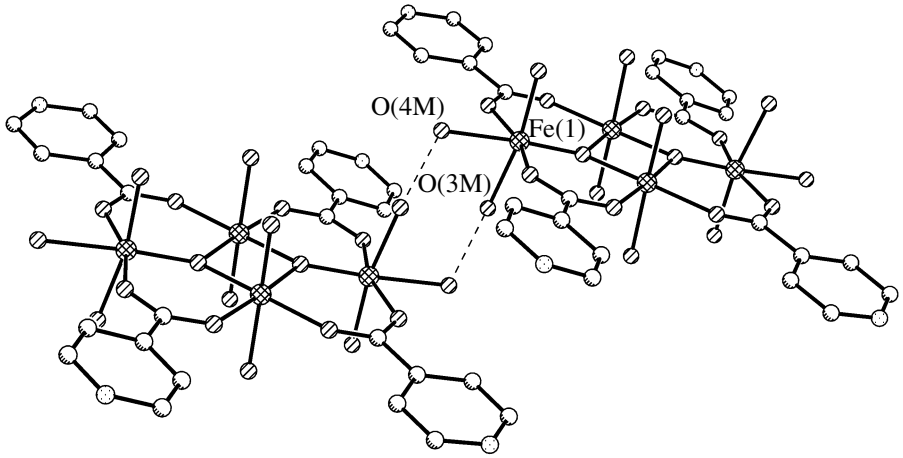


Fig. 2. Joining of the $[Fe_4O_2(H_2O)_{10}(C_5H_5NCOO)_4]^{8+}$ cations into chains along the *z* axis by hydrogen bonding (dash).

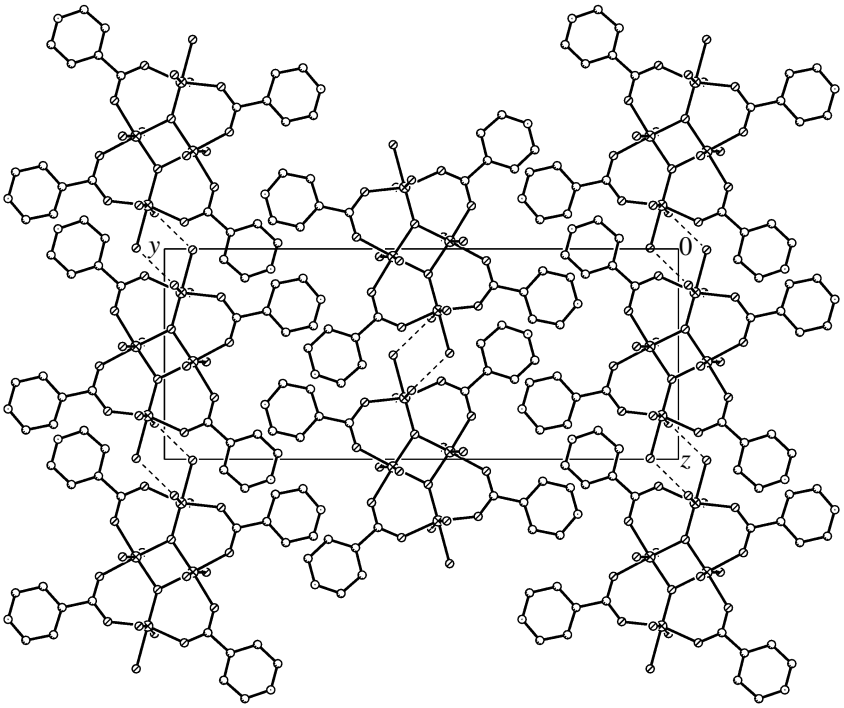


Fig. 3. Crystal packing in structure **I** in projection onto the *zy* plane. Hydrogen bonds are shown by dash. Hydrogen atoms, molecules of water of crystallization, and nitrate anions are omitted.

Thus, in the present work, we synthesized the new tetranuclear iron complex with the 4-pyridinecarboxylate anions and the planar Fe_4O_2 fragment. The tetranuclear iron complex is interesting as a promising compound for use as a building block in design of heterometallic coordination polymers due to the nitrogen atoms of the pyridine rings of the ligands accessible for coordination by transition metals.

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REFERENCES

1. Theil, E.C., *Annu. Rev. Biochem.,* 1987, vol. 56, p. 289.
2. Lippard, S.J., *Angew. Chem. Int. Ed.,* 1988, vol. 27, p. 344.
3. Waldo, G.S. and Theil, E.C., *Comp. Supramol. Chem.*, 1996, vol. 5, p. 65.
4. Brechin, E.K., Knapp, M.J., Huffman, J.C., et al., *Inorg. Chim. Acta*, 2000, vol. 297, p. 389.
5. Powell, A.K., Heath, S.L., Gatteschi, D., et al., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 2491.
6. Ruckstossfreie, R.L., *Kernresonanzabsorption Von Gammastrahlung.* Nobelvortrag 1961, Le Prix Nobelen 1961, Stockholm: Impremerie Royale P.A. Norstedt & Suner, 1962, p. 136.
7. Gol'danskii, V.I., *Effekt Messbauera* (Mössbauer Effect), Moscow: Akad. Nauk SSSR, 1963.
8. Mössbauer, R.L., *Usp. Fiz. Nauk*, 1960, vol. 72, no. 4, p. 658.
9. Christou, G., Gatteschi, D., Hendrickson, D.N., et al., *MRS Bull.*, 2000, vol. 25, p. 1.
10. *Bruker Advanced X-ray Solutions,* Bruker AXS Inc, Madison (WI, USA), 2004.
11. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
12. Kazitsyna, L.A. and Kupletskaya, N.B., *Primenenie UF-, IK-, YaMR- i mass- spektroskopii v organicheskoi khimii* (Use of UV, IR, NMR, and Mass Spectroscopy in Organic Chemistry), Moscow: Mosk. Gos. Univ., 1979.
13. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986, p. 227.
14. Ponomarev, I.V., Atovmyan, L.O., Bobkova, S.A., et al., *Dokl. Akad. Nauk SSSR*, 1984, vol. 274, p. 368.
15. Armstrong, W.H., Roth, M.E., and Lippard, S.J., *J. Am. Chem. Soc.*, 1987, vol. 109, p. 6318.
16. McCusker, J.K., Vincent, J.B., Schmitt, E.A., et al., *J. Am. Chem. Soc.*, 1991, vol. 113, p. 3012.
17. Chaudhuri, P., Winter, M., Fleischhauer, P., et al., *Inorg. Chim. Acta*, 1993, vol. 212, p. 241.
18. Wu, L., Pressprich, M., Coppens, P., et al., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, vol. 49, p. 1255.
19. Gorun, S.M. and Lippard, S.J., *Inorg. Chem.*, 1988, vol. 27, p. 149.