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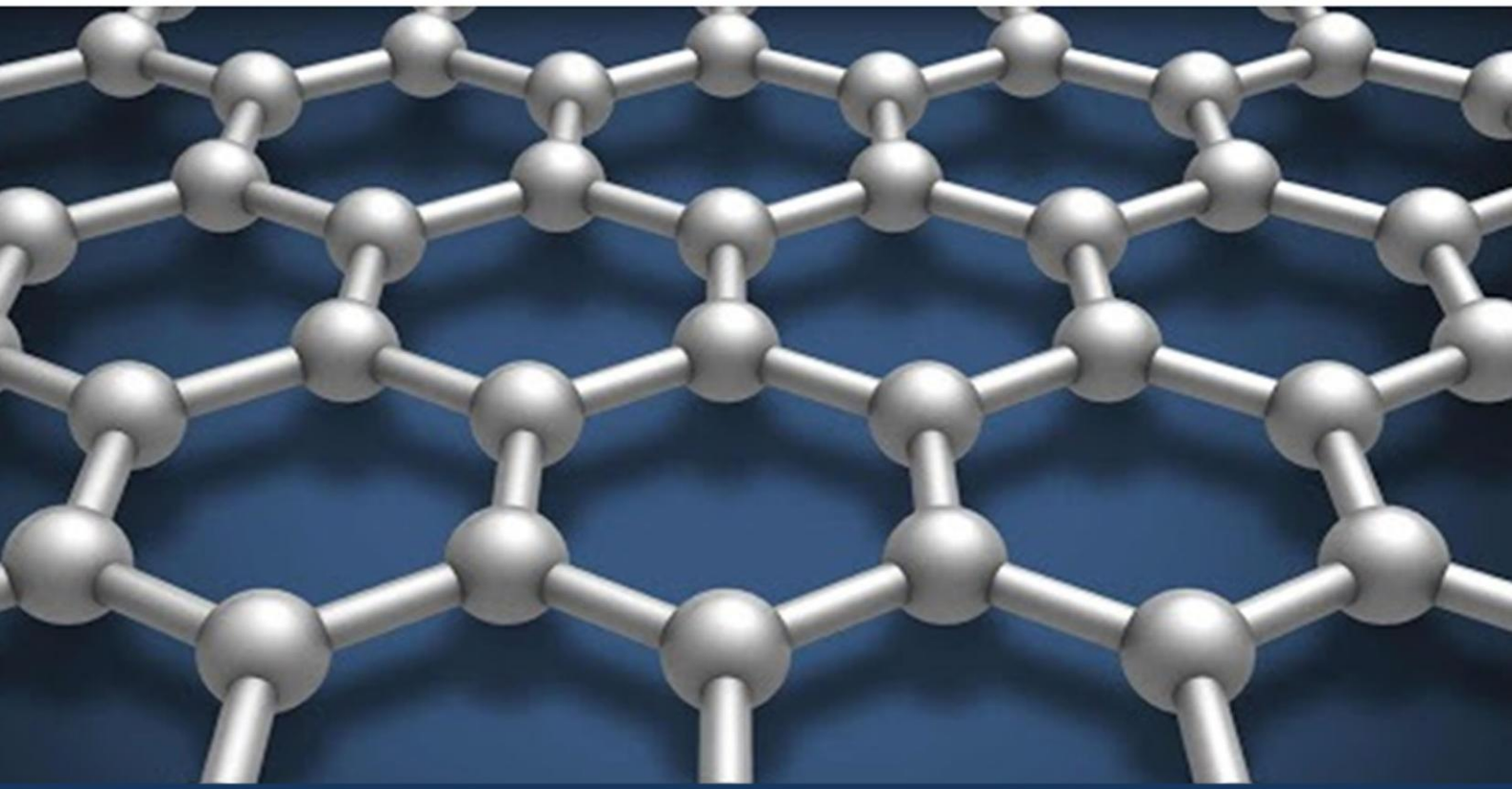

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CRYSTAL STRUCTURE AND UV–VIS SPECTROSCOPIC CORRELATION OF [TRIAQUA-μ$_3$-OXIDO-HEXA(3-HYDROXYBENZOATO)TRIIRON(III)] CHLORIDE DIHYDRATE

Ruzmetov A.Kh., Ibragimov A.B., Atajanov B.A.

Institute of General and Inorganic Chemistry, Academy of Sciences of Uzbekistan

Abstract. A new iron(III) coordination complex, $[Fe_3(O)(C_7H_5O_3)_6(H_2O)_3]\cdot Cl\cdot 2H_2O$ (Compound 1) has been synthesized and structurally characterized. The compound was obtained by the reaction of $FeCl_3\cdot 6H_2O$ with m-hydroxybenzoic acid under mild hydrothermal conditions. The complex crystallizes in a triclinic system, forming a trinuclear iron core bridged by a central μ$_3$-oxo atom and six m-hydroxybenzoate ligands. The molecular structure, hydrogen-bonding network, and supramolecular packing were elucidated using single-crystal X-ray diffraction analysis.

Keywords: trinuclear, crystal structure, hydrothermal synthesis, hydrogen bonds.

Introduction. Hydroxybenzoic acids and their metal complexes have attracted considerable attention due to their structural flexibility, biological activity, and coordination ability. Among them, **3-hydroxybenzoic acid (m-hydroxybenzoic acid)** is a naturally occurring phenolic compound found in plants such as grapefruit, olive oil, and medlar fruit. It is widely applied in pharmaceuticals, cosmetics, and food preservation because of its antimicrobial and antioxidant properties [1]. The presence of both carboxylic and phenolic functional groups allows this ligand to form stable coordination compounds with transition metals, often enhancing its biological and catalytic behavior [2]. Recent crystallographic and thermodynamic studies have revealed that 3-hydroxybenzoic acid can exist in several polymorphic forms that differ in hydrogen-bonding motifs, significantly affecting its physicochemical stability and reactivity [3,4]. Owing to these structural characteristics and its ability to coordinate through the carboxyl oxygen, it serves as a useful model compound for exploring structure-property relationships in coordination chemistry. Furthermore, hydroxybenzoic acids play an important biological role as antioxidants and enzyme modulators, contributing to the prevention of cardiovascular and metabolic disorders [5].

Iron coordination complexes have attracted great interest due to their diverse structural motifs and potential applications in catalysis, magnetism, and bioinorganic chemistry. Carboxylate ligands, particularly hydroxybenzoates, are known to form robust frameworks and contribute to rich coordination geometries around the metal centers. In this study, we report the synthesis and crystal structure of a new trinuclear iron(III) complex, $[Fe_3(O)(C_7H_5O_3)_6(H_2O)_3]\cdot Cl\cdot 2H_2O$, obtained from the reaction of $FeCl_3\cdot 6H_2O$ with m-hydroxybenzoic acid.

Experimental Section. Reflection sets for X-ray diffraction experiments were obtained at 293 K on an XtaLAB Synergy, single source at home/near, HyPix3000 diffractometer (micro-focus sealed X-ray tube, PhotonJet (Cu (λ=1.54184 Å), X-ray Source Mirror monochromator, Detector resolution 10.0000 pixels mm^{-1}, *ω*-scans). Experimental data were collected using the CrysAlisPro program [6]. An absorption correction was applied by the multi-scan method in the same program. The structure was solved by the direct method using the SHELXT program package [7] and refined by full-matrix least squares using the SHELXL program [8]. All non-hydrogen atoms were refined anisotropically. The molecular drawings were plotted by MERCURY program package [9]. The crystallographic data and details of the structure refinement are given in Table 1.

All reagents were of analytical grade and purchased from Sigma-Aldrich. A solution of $FeCl_3\cdot 3H_2O$ (1 mmol, 0.270 g) was prepared in acetonitrile (20 mL). Separately, m-hydroxybenzoic acid (2 mmol, 0.276 g) was dissolved in ethanol (20 mL) with gentle heating. The ligand solution was then added dropwise to the metal salt solution under continuous magnetic stirring. The reaction mixture was stirred for 1 h at 40 °C to ensure complete homogenization. The resulting clear brown solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, filled to 40 mL of its total volume, and heated hydrothermally at 110 °C for 24 h. After slow cooling to room temperature, the solution was left in a partially covered beaker with a small perforation to allow slow evaporation. Over the course of two weeks, brown single crystals suitable for X-ray diffraction analysis were formed. The crystals were collected by filtration, washed with diethyl ether, and air-dried. The yield was approximately 60%. Elemental analysis calculated (in %): C - 44.57%; H - 3.56%; O - 33.93%; Fe - 14.80%. Found (in %): C - 43.82%; H - 3.41%; O - 33.02%; Fe - 14.35%.

Table 1.

Cell parameters of the Compound 1

Parameter	Value
Chemical formula	$C_{42}H_{36}Fe_3ClO_{25}$
Formula weight	1116.26
Crystal system	Tetragonal
Space group	P 42/n
a (Å)	24.9665(6)
b (Å)	24.9665(6)
c (Å)	15.3163(6)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	9547.0(6)
Z	8
Density (calc.) (g·cm^{-3})	1.553
μ (mm^{-1})	8.007
F(000)	4560
Crystal habit	Plate
Temperature (K)	293
Measured reflections	9682
θ max (°)	76.99
R1 [I > 2σ(I)]	0.0983
R1 (all data)	0.1452
wR2 (all data)	0.3180
Largest diff. peak / hole (e Å^{-3})	+3.792 / -0.708

Results and discussion. The crystal structure reveals a triangular arrangement of three Fe(III) ions linked through a central μ$_3$-oxo atom. Each Fe(III) ion is octahedrally coordinated by oxygen atoms from the m-hydroxybenzoate ligands and one water molecule (Fig. 1). The Fe-O bond lengths are within the typical range for high-spin Fe(III) centers (Tab. 2). The carboxylate groups act as bridging ligands, linking the metal centers into a stable trinuclear core.

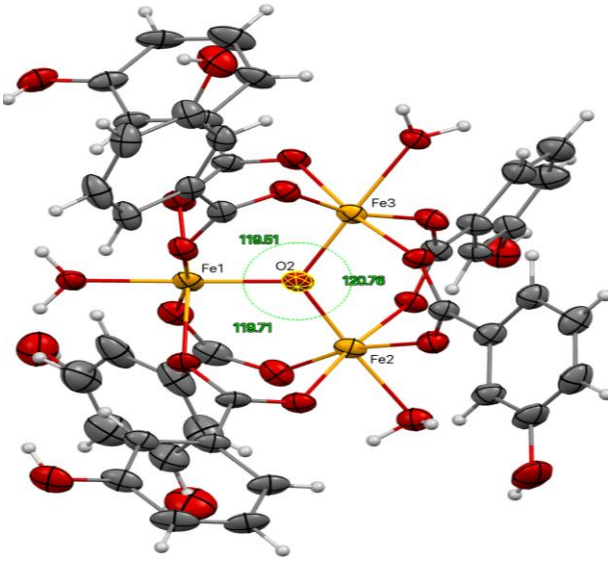

Fig. 1. The crystal structure of the compound 1 (probability 25%)

The crystal packing is stabilized by an extensive network of O-H···O hydrogen bonds involving coordinated and lattice water molecules, forming a three-dimensional supramolecular framework. The Fe-O-Fe bond angles in the complex are nearly identical. This indicates that the three iron atoms are positioned almost symmetrically around the central oxygen atom, forming approximately 120° angles with each other (Tab. 2).

Table 2.

Distances between iron and oxygen atoms

Fe-O distances (Å)	Bond length	Fe-O2-Fe	Angle°
Fe(1) - O(1)	1.96(2) Å	Fe1-O2-Fe3	119,51
Fe(1) - O(3)	2.02(3) Å	Fe3-O2-Fe2	120,76
Fe(2) - O(5)	1.99(2) Å	Fe2-O2-Fe1	119,71
Fe(3) - O(7)	2.04(3) Å		
Fe - O	2.00 Å		

UV-Vis Spectral Analysis. Electronic transitions in the compound were investigated using UV-spectrophotometric technique (Cary 5000 UV-Vis-NIR Agilent Technologies) in the wavelength range of 200-1100 nm. A 0.05 molar solution of the complex was prepared, dissolved in C_2H_5OH (96%), and its electronic transition events were analysed (Fig. 2). The UV-Vis absorption spectrum of the trinuclear iron(III) complex $[Fe_3(O)(C_7H_5O_3)_6(H_2O)_3]\cdot Cl\cdot 2H_2O$ (in ethanol) is characterized by a strong band in the ultraviolet region (~290 nm) and an essentially featureless visible region. Notably, no d-d transition bands are observed in the visible range. This absence is expected for high-spin Fe^{3+} (d^5) centers, since all ligand-field (d-d) transitions from the sextet ground state are spin-forbidden and therefore extremely weak [10]. In fact, for octahedral Fe(III) complexes, any d-d absorptions in the visible are very faint too weak to produce distinct peaks under standard conditions [11]. In some cases a barely perceptible shoulder around ~420-440 nm can be attributed to the spin-forbidden transitions of Fe^{3+}, but no such shoulder is apparent here, indicating that any Fe^{3+} d-d transitions are completely obscured by the baseline noise or overlapping with more intense bands.

The dominant ~290 nm band can be assigned to an intense charge-transfer transition involving the ligands and the Fe(III) centers. Oxygen-donor ligands (such as the mHBA carboxylate or phenolate oxygens, or the μ$_3$-oxo bridge) can undergo ligand-to-metal charge transfer (LMCT) to Fe^{3+}, resulting in UV-range absorption. In

analogous Fe(III)-O systems, broad charge-transfer bands occur below ~300 nm and are attributed to O(2p)→Fe^{3+} (3d) transitions [3]. Such LMCT bands have high oscillator strength, consistent with the intensity of the ~290 nm peak. The mHBA ligands' aromatic π-π* transitions also typically lie in the UV range and may contribute to the absorption around 290 nm. However, the observed band's strength and the complete lack of any lower-energy (visible) peaks strongly suggest that a ligand-to-Fe(III) charge transfer is the primary electronic transition in this complex.

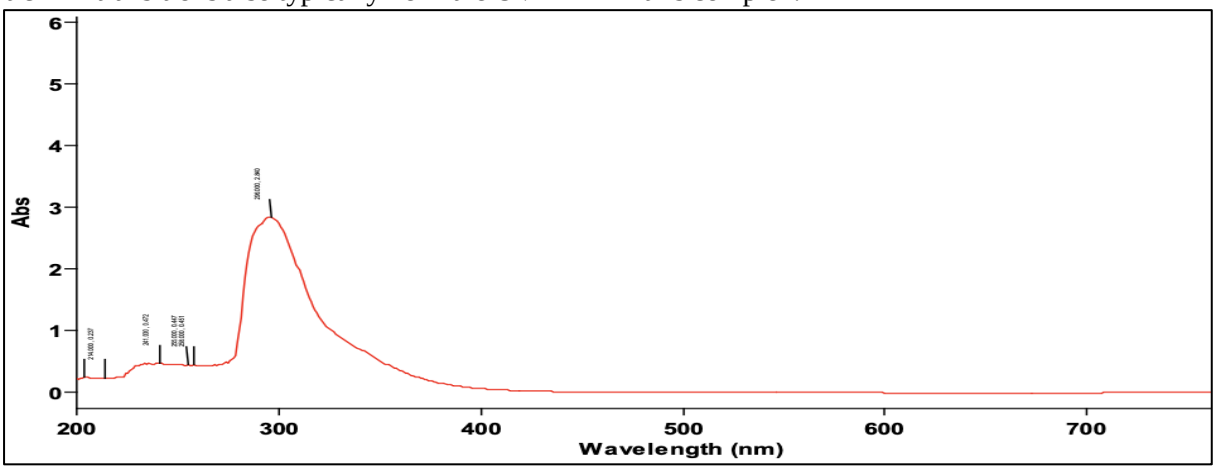

Fig. 2. UV spectrum of the $[Fe_3(O)(C_7H_5O_3)_6(H_2O)_3]\cdot Cl\cdot 2H_2O$

Conclusion. A new trinuclear Fe(III) complex with m-hydroxybenzoate ligands, $[Fe_3(O)(C_7H_5O_3)_6(H_2O)_3]\cdot Cl\cdot 2H_2O$, has been synthesized and characterized by single-crystal X-ray diffraction. The complex exhibits a μ_3-oxo bridged Fe_3 core with octahedral coordination geometry. Hydrogen bonding and π-π interactions contribute to the stability of the crystal packing. This structure provides new insight into the assembly of iron-carboxylate systems and their supramolecular architectures.

The UV-Vis spectrum of the complex exhibits a strong absorption band near 290 nm, attributed to ligand-to-metal charge transfer (LMCT) transitions from oxygen donor atoms of m-hydroxybenzoate and μ_3-oxo groups to the Fe^{3+} centers. The absence of visible-region d-d transitions is consistent with the high-spin d^5 configuration of Fe^{3+}, for which such transitions are spin-forbidden and of very low intensity. This observation agrees with previously reported spectra of Fe(III) carboxylate systems, suggesting that electronic behavior is dominated by LMCT processes. The structural symmetry and antiferromagnetic nature of Fe-O-Fe interactions further reinforce this interpretation.

In conclusion, the combination of crystallographic and spectroscopic data confirms the successful synthesis of a stable trinuclear Fe(III) complex exhibiting both structural and electronic characteristics typical of μ_3-oxo bridged iron clusters. The results highlight the role of m-hydroxybenzoate ligands in stabilizing trinuclear frameworks and demonstrate their importance in controlling the charge-transfer properties of Fe(III) coordination compounds. This work provides valuable insights into structure-property relationships relevant to the design of new coordination materials.

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