



*Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 85th anniversary*

A DINUCLEAR IRON(III) COMPLEX BRIDGED BY THE DIANION OF TRIMESIC ACID – [$\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}_2\text{Htrim}\} \cdot \text{H}_2\text{O}$]: SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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A neutral dinuclear iron(III) complex, [$\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}_2\text{Htrim}\} \cdot \text{H}_2\text{O}$ **1**, has been synthesized by reacting the mononuclear iron(III) complex [$\text{Fe}(3\text{-MeOsaldmpn})\text{Cl}(\text{H}_2\text{O})$] with trimesic acid in the presence of LiOH. Compound **1** was structurally characterized by X-ray diffraction on single crystal. The Schiff-base ligand was obtained by reacting *o*-vanillin with 2,2-dimethyl-1,3-diaminopropane. The iron(III) ions, within the neutral dinuclear complex, are bridged by the dianion of trimesic acid, with an intramolecular Fe...Fe separation of 11.12 Å. Each iron(III) in **1** is six-coordinated in a somewhat distorted octahedral coordination mode. The cryomagnetic investigation of **1** reveals a weak antiferromagnetic coupling of the iron(III) ions ($J = -0.12 \text{ cm}^{-1}$, $\mathbf{H} = -J\mathbf{S}_{\text{Fe1}}\mathbf{S}_{\text{Fe1}}$).

INTRODUCTION

Polynuclear complexes containing paramagnetic metal ions are currently of interest in the field of molecular magnetism and materials chemistry due to their fascinating structural diversities and potential applications.¹ Bridging ligands have been shown to transmit magnetic interactions in addition to the simple binding of metal centers into specific coordination geometries. As bridging ligands, carboxylates, especially poly-carboxylates, are of high interest in the construction of polymeric coordination architectures owing to the fact that these polymers, with a wide range of structural diversities, have potential applications as porous materials and magnetic materials.^{2,3} The multidentate aromatic polycarboxylato ligands have been extensively employed in the construction of a rich variety of high-dimensional structures.^{4,5} It is well known that

organic ligands play a rather important role in the construction of MOFs, and multicarboxylato ligands are frequently chosen owing to their rich coordination modes (coordinating to metal ions through complete or partial deprotonation of their carboxylic groups) and their metal bridging ability.⁶⁻¹¹

Among the aromatic carboxylates, trimesic acid has been extensively employed as linker for the generation of both high nuclearity clusters and 1D, 2D, and 3D coordination polymers.¹² The case of trimesic acid is particularly interesting as it has three carboxyl groups, which can be fully or partially deprotonated to generate a variety of structural topologies. In this paper we report the synthesis, crystal structure and the magnetic properties of a novel dinuclear iron(III) complex bridged by the dianion of trimesic acid [$\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}_2\text{Htrim}\} \cdot \text{H}_2\text{O}$ (**1**) [3-MeOsaldmpn²⁻ = *N,N'*-dimethylpropylenebis(3-methoxysalicylideneimine)].

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EXPERIMENTAL

Materials and Methods

Anhydrous iron(III) chloride, *o*-vanillin, 2,2-dimethyl-1,3-diaminopropane, trimesic acid, lithium hydroxide and the acetonitrile solvent were purchased from commercial sources and used as received. The mononuclear iron(III) precursor [Fe(3-MeOsaldmpn)Cl(H₂O)] was prepared by using the same method as reported by us for mononuclear [Fe(3-MeOsalp)Cl(H₂O)] complex.¹³

Preparation of the [Fe(3-MeOsaldmpn)(H₂O)₂Htrim]·H₂O (1) Complex

A solution of trimesic acid (10.5 mg, 0.05 mmol) and lithium hydroxide (6.2 mg, 0.15 mmol) in 20 mL (1:1) mixture of CH₃CN and H₂O was added to a 20 mL CH₃CN solution of mononuclear iron(III) precursor [Fe(3-MeOsaldmpn)Cl(H₂O)] (23.8 mg, 0.05 mmol). The resulting dark brown colored solution was stirred for 1 hour at room temperature and subsequently filtered. The filtrate was left to evaporate at room temperature in a hood. Well shaped brown prisms of **1** were formed after two weeks. They were filtered, washed with small amounts of cold water and dried on filter paper. Yield (after different crops of crystals): *ca.* 90 %. Selected IR data (KBr pellets/cm⁻¹): 3436(m,br), 2932(m,br), 1613(vs), 1551(m), 1470(m), 1438(m), 1390(m), 1307(m), 1248(s),

1225(m), 1170(w), 1067(m), 969(w), 859(m), 742(m), 639(w), 557(w), 456(w).

Physical Techniques

The IR spectra (KBr pellets) were collected on a Bruker Tensor 37 spectrophotometer in the 4000–400 cm⁻¹ range. UV–Vis spectra (diffuse reflectance technique) were recorded on a JASCO V-670 spectrophotometer, using MgO as a standard. Variable temperature (2.0–300 K) magnetic susceptibility measurements were carried out on polycrystalline samples with a MPMS SQUID magnetometer by applying a 1500 G external magnetic field.

X-ray Crystallographic Analysis

X-ray diffraction measurements were performed on a STOE IPDS II diffractometer operating with Mo K α ($\lambda = 0.71073$ Å) X-ray tube with a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package.¹⁴ The graphical manipulations were carried out with the DIAMOND program.¹⁵ A summary of the crystallographic data and the structure refinement for crystal **1** is given in Table 1 whereas main bond lengths are listed in Table 2.

Table 1

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

Compound	1
Chemical formula	C ₅₁ H ₆₂ Fe ₂ N ₄ O ₁₉
<i>M</i> (g mol ⁻¹)	1146.75
Temperature, (K)	293(2)
Wavelength, (Å)	0.71073
Crystal system	<i>Monoclinic</i>
Space group	<i>C2/c</i>
<i>a</i> (Å)	23.6519(17)
<i>b</i> (Å)	11.1888(5)
<i>c</i> (Å)	20.2084(14)
α (°)	90
β (°)	97.762(6)
γ (°)	90
<i>V</i> (Å ³)	5298.9(6)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.437
μ (mm ⁻¹)	0.627
<i>F</i> (000)	2400
Goodness-of-fit on F^2	1.029
Final <i>R</i> 1, <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0588, 0.0964
<i>R</i> 1, <i>wR</i> ₂ (all data)	0.1048, 0.1087
Largest diff. peak and hole (eÅ ⁻³)	0.962, -0.347

Table 2

Selected bond distances (Å) for complex **1**

Fe1-N1	2.137(3)
Fe1-N2	2.124(3)
Fe1-O2	1.920(2)
Fe1-O3	1.919(2)
Fe1-O8w	2.093(3)
Fe1-O6	2.045(2)
Fe1-Fe1'	11.124

' = 2-x, y, 1.5-z

RESULTS AND DISCUSSION

Synthesis and Characterization

The dinuclear iron(III) complex $[\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}_2\text{Htrim}]\cdot\text{H}_2\text{O}$ **1** has been prepared by reacting the mononuclear iron(III) compound $[\text{Fe}(3\text{-MeOsaldmpn})\text{Cl}(\text{H}_2\text{O})]$ with trimesic acid in a 2:1 mole ratio in which the chloride ion in each of the two molecules of mononuclear iron(III) precursor is replaced by the two deprotonated carboxylic groups, in a monodentate mode, of the trimesic acid. The third carboxylic group remains protonated giving overall a neutral complex. A broad and medium intensity absorption band at 3436 cm^{-1} in the IR spectrum is attributed to the presence of water molecules coordinated in the axial position of two iron(III) moieties, as well as to the crystallization water molecule. The presence of the three carboxyl groups in the bridging dianion of the trimesic acid is evidenced by the appearance of strong i.r. peak at 1613 cm^{-1} . The appearance of a splitted peak around 2930 cm^{-1} can be assigned to two methyl and methylene groups in the Schiff-base of two iron(III) moieties. All these structural features have been confirmed by the crystal structure of **1** (see below).

Description of the Structure of $[\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}_2\text{Htrim}]\cdot\text{H}_2\text{O}$ **1**

The crystal structure of **1** (Fig. 1) consists of neutral $[\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}_2\text{Htrim}]\cdot\text{H}_2\text{O}$ dinuclear species, the two $\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}$ moieties being connected by the dianion of the trimesic acid in which the two deprotonated carboxylic groups are coordinated in a monodentate bridging mode into the axial position of the two iron(III) ions. The third carboxylic group remains protonated giving overall a neutral complex. Each iron(III) in **1** is six-coordinated in a somewhat distorted octahedral coordination mode. The basal plane is formed by two nitrogen atoms [$\text{Fe1} - \text{N1} = 2.137(3)$; $\text{Fe1} - \text{N2} = 2.124(3)\text{ \AA}$] and two phenolato oxygens [$\text{Fe1} - \text{O2} = 1.920(2)$; $\text{Fe1} - \text{O3} = 1.919(2)\text{ \AA}$] of the Schiff-base. The apical positions are occupied by one water molecule [$\text{Fe1} - \text{O8W} = 2.093(3)\text{ \AA}$] and one oxygen atom [$\text{Fe1} - \text{O6} = 2.045(2)\text{ \AA}$] from one carboxylato group of the bridging trimesate dianion. The Schiff-base in each of the two $\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}$ moieties is twisted, with the dihedral angle between the mean planes of *o*-vanillin Schiff base of 46.5° . The 3d metal ion is

hosted into the inner (N_2O_2) compartment of the bicompartamental ligand. This type of mononuclear complexes, with a metal ion hosted into the N_2O_2 compartment, shows an interesting property: the second compartment, $\text{O}_2\text{O}'_2$, can act as a good receptor not only toward metal ions, but also toward hydrogen bond donors.¹⁶ This feature is also observed for the binuclear iron(III) complex, the outer $\text{O}_2\text{O}'_2$ compartments hosting crystallization water molecules (Fig. 2). Each hydrogen atom of the water molecule forms bifurcated hydrogen bonds with one phenoxo and one methoxy oxygen atoms. The $\text{O}\cdots\text{O}$ distances are: $\text{O1}\cdots\text{O9W}'' = 2.920$, $\text{O2}\cdots\text{O9W}'' = 3.258$, $\text{O3}\cdots\text{O9W}'' = 3.036$, $\text{O4}\cdots\text{O9W}'' = 3.034\text{ \AA}$ (symmetry code: '' = $1.5-x, -0.5-y, 1-z$). The crystallization water molecules hosted in the $\text{O}_2\text{O}'_2$ compartments act as hydrogen bond acceptors for water molecules coordinated to metal ions of the neighbouring complexes generating supramolecular chains ($\text{O8W}\cdots\text{O9W} = 2.690\text{ \AA}$ – Fig. 2).

The intramolecular $\text{Fe}\cdots\text{Fe}$ separation between the two $\{\text{Fe}(3\text{-MeOsaldmpn})(\text{H}_2\text{O})\}$ moieties of the dinuclear complex is equal to 11.12 \AA .

Magnetic Properties

The cryomagnetic properties of the complex **1** have been investigated in the $2 - 300\text{ K}$ temperature range. The $\chi_{\text{M}}T$ vs. T curve for complex **1** [χ_{M} is the magnetic susceptibility per a pair of iron(III) ions] is shown in Fig. 3. At room temperature, the value of the $\chi_{\text{M}}T$ product is $8.70\text{ cm}^3\text{ mol}^{-1}\text{ K}$. This value is close to the expected one for two magnetically isolated high-spin iron(III) ions (ca. $8.75\text{ cm}^3\text{ mol}^{-1}\text{ K}$ with $S_{\text{Fe}} = 5/2$ and $g = 2.0$). Upon cooling, $\chi_{\text{M}}T$ for the complex remains practically constant down to 200 K , and then it further decreases continuously to reach a value of $5.53\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 2.0 K . This decrease in the low temperature range for **1** is due to weak antiferromagnetic interactions mediated by the trimesato bridge.

The magnetic data are analyzed by using the isotropic spin Hamiltonian for a simple binuclear complex:

$$\mathbf{H} = -J\mathbf{S}_{\text{Fe1}}\mathbf{S}_{\text{Fe1}'}$$

The best fit to the data leads to the following set of parameters: $g = 1.93$; $J = -0.12\text{ cm}^{-1}$.

The low value of exchange coupling constant is due to large distance, imposed by the polycarboxylato trimesate dianion, between two iron(III) ions in the neutral dinuclear complex **1**.

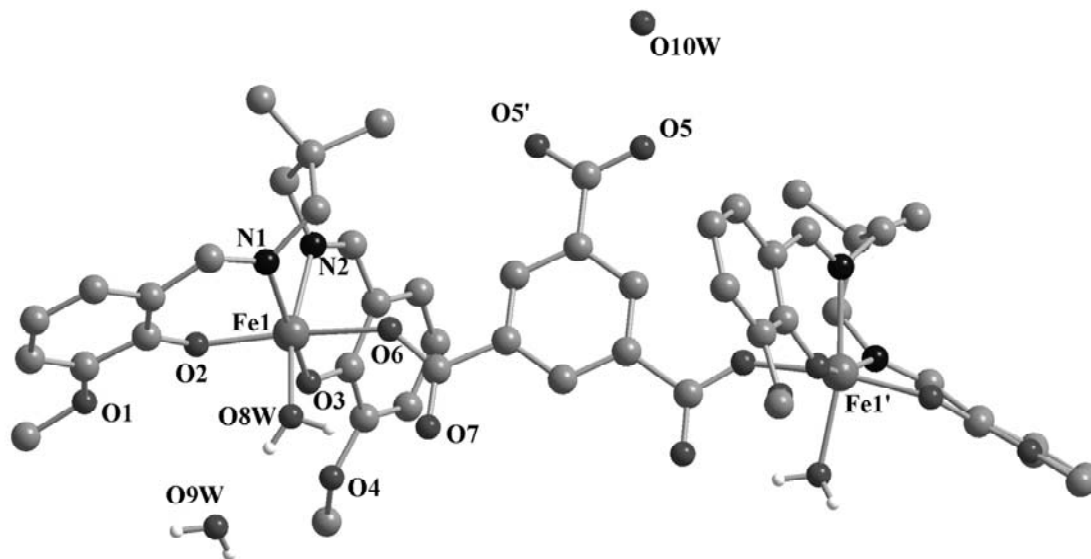


Fig. 1 – Perspective view of $[\{\text{Fe}(\text{3-MeOsaldmpn})\text{H}_2\text{O}\}_2\text{Htrim}] \cdot \text{H}_2\text{O}$ (1).

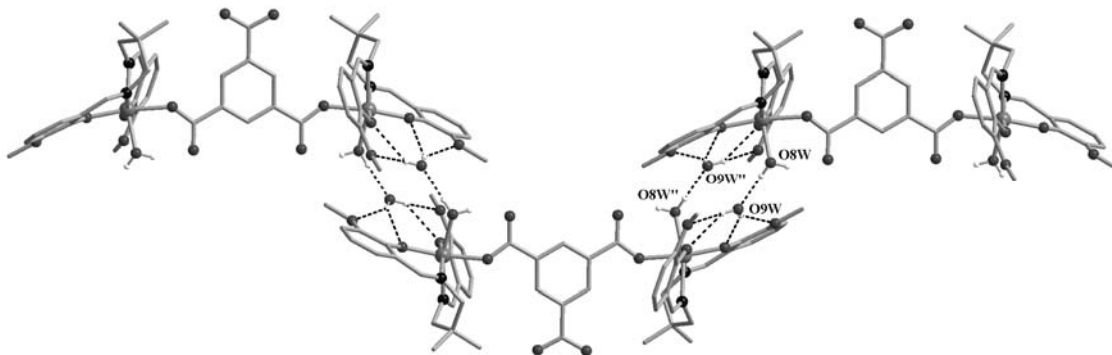


Fig. 2 – Perspective view of the supramolecular chains generated by hydrogen bond interactions.

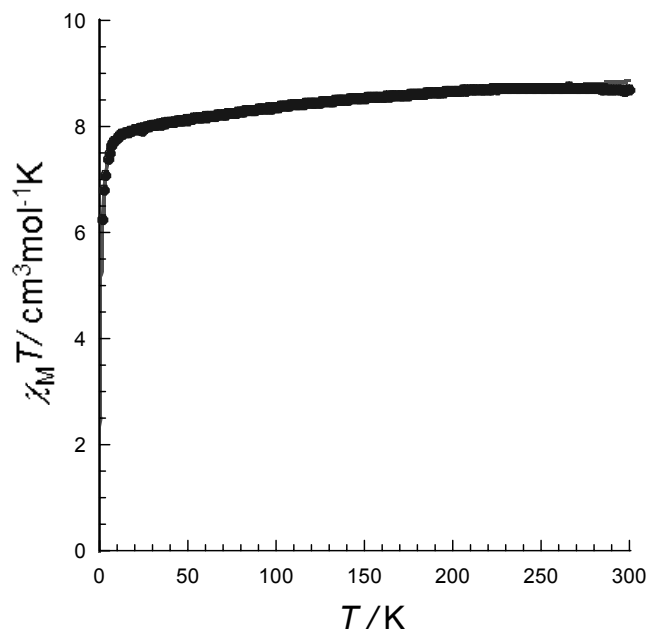


Fig. 3 – The $\chi_M T$ vs. T curve for complex 1. The solid line represents the best fit to the data.

CONCLUSION

In conclusion, we have demonstrated with a new example the richness of the chemistry generated by polycarboxylato ligands acting as bridges. The case of the trimesato complexes is quite interesting, as mentioned in the introduction and illustrated by complex **1**, that in addition to the coordination polymers, discrete complexes can be generated by employing Schiff-bases as blocking ligands for the metal ions.

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Appendix A. Supplementary material

CCDC 861098 contains 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/data_request/cif.

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