

## A New Method of Preparation, Abinitio Calculation and Description of Infrared Spectrum of $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$

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### Abstract

The complex  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$  was prepared by treating 1, 3, 5-trimethyl-2, 4, 6-trioxane with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in the presence of sodium metal. The structure of this complex was calculated by abinitio method as a Hexagonal skeleton with bridging - acetate ion. Based on this calculation  $D_{3h}$  symmetry for the central  $\text{Fe}_3\text{O}$  unit, and  $C_{2v}$  symmetry for trans- $\text{Fe O}''\text{O}_4$  - units chelated on iron ions around the three centred nuclei, are proposed. Combination vibration of these two units resulted in explanation and characterization of IR spectrum of this compound.

### Introduction

Multi-centered complexes of symmetrical (syn-syn) bridged acetate ligands with different transition metals have attracted the interest of several groups in the past few decades.<sup>1-3</sup> Among them, complexes of the type  $[\text{M}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]\text{X} \cdot n\text{H}_2\text{O}$ , where, X is a halogen and M is Fe, Cr, ..., having an oxide ion in center of a triangle generated by the three metal ions are also known.<sup>4</sup> Synthesis of acidic and dianionic salts such as alkali hydrogen diacetate is reported by the reaction of alkali metals with 1, 3, 5-trimethyl-2, 4, 6-trioxane as the starting material.<sup>5</sup> Now a new simple method is proposed for one pot preparation of chlorinated  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$  by treating  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with the above methylated trioxane. Then, the results on the characterization and interpretation of IR spectrum of this compound are introduced in a new point of view.

## Experimental Section

One hundred ml of freshly distilled 1, 3, 5-trimethyl-2, 4, 6-trioxane was placed in a three-necked round bottomed flask (250ml) equipped with a reflux condenser, magnetic stirrer, and air bubbler. By heating the content to 50°C and air bubbling, 0.05 mol (13.5 g) FeCl<sub>3</sub>·6H<sub>2</sub>O and 5.7 g sodium metal was gradually added and the resulting mixture was refluxed at 75°C for 4h. The precipitate washed with iso-octane. A brownish-red powder (6.7 g, 65% yield) with the elemental analysis as follows Cl(5.5%), H(3.6%), C(22.9%) and Fe(26.6%), which identified as [Fe<sub>3</sub>O(AcO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl was obtained. (6.7 g) with 65% yield. Infrared spectrum of [Fe<sub>3</sub>O(AcO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> is shown in Fig. 2.

## Results and discussion

The molecular structure of this iron complex were calculated by abinitio method at room temperature and Helium atmosphere. These calculation were performed on two various systems namely UHF/6-31 G<sup>\*\*</sup> and LSDF/6-31 G<sup>\*\*</sup>. A perspective view of the molecular structure of this complex is depicted in Figure 1. Selected bond distances and angles are listed in Table 1. These values showed that the central O-atom is positioned on the plane defined by the three iron atoms. The central Fe<sub>3</sub>O atoms formed an triangle array with 120° angle and D<sub>3h</sub> symmetry. The bond distances between each iron and central oxide ion (O'-Fe) is 1, 8375 Å and between Fe and oxygen of to water ligand (Fe-O") is 1, 8021 Å, and each Fe ion has a distorted octahedral array as FeO'O"O<sub>4</sub>. Thus the angle values O<sub>1</sub>-Fe-O<sub>2</sub>(88.815deg.) and O<sub>2</sub>-Fe-O<sub>3</sub>(91,319 deg.) confirm a C<sub>2v</sub> skeleton for MO<sub>1</sub>O<sub>2</sub>O<sub>3</sub>O<sub>4</sub> plain. The planes of the three H<sub>2</sub>O ligands are perpendicular to this plane.

Vibrational spectra of three centered oxo-carboxylates are discussed generally based on the vibrational behavior of particular units in molecule.<sup>10</sup> Clearly, all the three centred oxo-carboxylates show similar structure, but differ in the kind of nonacetate ligands. Infrared and Raman vibrations of [Fe<sub>3</sub>O(AcO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> are discussed based on

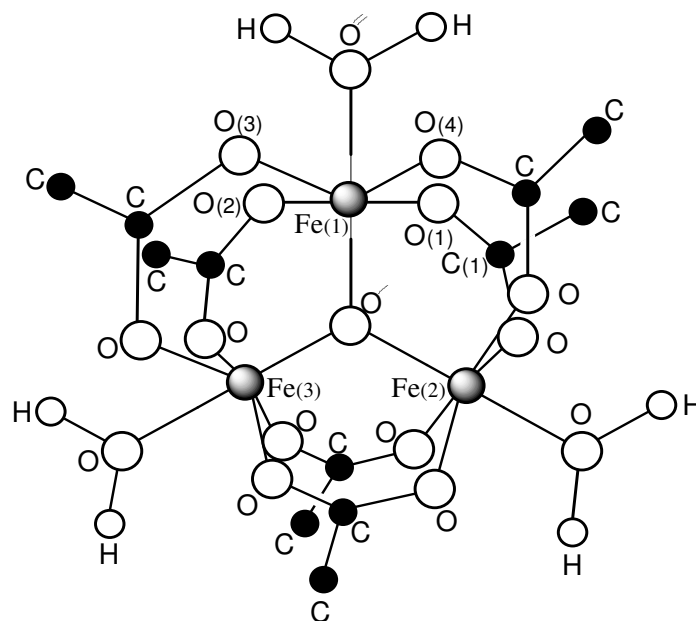
vibrations of units, which interact with each other and finally combine with vibrations of Fe<sub>3</sub>O as central triangle skeleton.

**Table 1. Abinitio calculation for selected distances (Å) and Angles. for complex [Fe<sub>3</sub>O(AcO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl.**

Mean value	LSDF/6-31G**	UHF/6-31G**	Band/Angel
O-C-O(deg)	123.582	124.901	124.241(deg)
Fe <sub>1</sub> -O'-Fe <sub>1</sub> (deg)	120	120	120(deg)
O'-Fe <sub>1</sub> -O <sub>1</sub> (deg)	96.360	94.512	95.371(deg)
	96.361	94.215	
O <sub>1</sub> -Fe <sub>1</sub> -O <sub>2</sub> (deg)	88.809	88.801	88.815(deg)
O <sub>2</sub> -Fe <sub>1</sub> -O <sub>3</sub> (deg)	91.081	91.198	91.139(deg)
Fe <sub>1</sub> -O <sub>1</sub> -C <sub>1</sub> (deg)	132.107	130.100	131.136(deg)
Fe <sub>1</sub> -O' (Å)	1.8230	1.8520	1.8375 (Å)
Fe <sub>1</sub> -O <sub>1</sub> (Å)	1.9893	1.9625	1.9759 (Å)
C <sub>1</sub> -O <sub>1</sub> (Å)	1.2359	1.2097	1.2228 (Å)
Fe <sub>1</sub> -O" (Å)	1.8021	1.8853	1.8437 (Å)
Fe <sub>1</sub> -Fe <sub>2</sub> (Å)	3.2881	3.2790	3.2836 (Å)

Grifit<sup>6</sup> pointed out, vibrational spectrum of molecule is the result of interaction of central Fe<sub>3</sub>O unit with D<sub>3h</sub> symmetry and its surrounding with D<sub>4h</sub> symmetry. Jhonson<sup>7</sup> believes that final vibration of molecule is the result of vibrations of FeO<sub>4</sub> side units with C<sub>4v</sub> symmetry and central Fe<sub>3</sub>O triangle with D<sub>3h</sub> symmetry. According to the general structure of molecule in Fig. 1, FeO<sub>4</sub> side units and Fe<sub>3</sub>O triangle are perpendicular to each other. We believe that final vibration of the general structure of this compound is the result of combination of vibrations of trans- FeO'O''O<sub>4</sub> units with C<sub>2v</sub> local symmetry with vibrations of central Fe<sub>3</sub>O skeleton with D<sub>3h</sub> local symmetry. This explanation is in accord with findings of Negro<sup>8</sup>, in which the angle of 124° – 125° calculated for acetate bridges with C<sub>2v</sub> symmetry. Grigorev<sup>9</sup> believes that vibrations in this angle depends on the kind of metal, increase in energy of ν<sub>3</sub> vibration, and decrease in energy of ν<sub>8</sub> vibration (Table 2). Considering Fig. 1. The atoms O<sub>1</sub>, O<sub>2</sub>, O<sub>3</sub> and O<sub>4</sub> are

homoplanar oxygens of four neighboring acetates (one oxygen atom from each acetate), O' oxygen of the central triangle, and O'' oxygen of water molecules. Thus Fe-O' and Fe-O'' bonds are distinct and the general skeleton of this ion is similar to a hexagon<sup>2,4,10-12</sup>.



**Figure 1. General Structure of [Hexa- $\mu$ -acetato- $\mu$ -trioxotriiron(III)].**

According to the above discussions,  $\text{FeO}'\text{O}''\text{O}_4$  unit should occupy a position with  $C_{2v}$  symmetry. Therefore, fifteen vibrational modes are proposed for this part of molecule<sup>13</sup>. Because of small anion-cation interactions in solid acetate compounds, no important changes are observed in the vibrational spectra of solid and liquid acetate compounds. Table 2 shows position of acetate vibrations in  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$ . Most important vibrations of this complex are due to CO,  $\text{CO}_2$ , and CC groups. These vibrations are also known in coordination compounds of acetates, which give useful structural informations about coordination of acetates in complexes with more than one acetate. In these compounds M-O vibration depends on the symmetry of molecule. Whose correlation between  $\text{MO}_4\text{O}'\text{O}''$  ( $C_{2v}$ ) and  $\text{M}_3\text{O}$  ( $D_{3h}$ ) vibrational modes and values are shown in Table 3 and 4. It should be noted that these vibrations split in their positions, as if acetate ions occupy similar surrounding<sup>14</sup>. According to IR spectrum of molecule in Fig. 2, most important vibrations in acetate are symmetric,  $\nu_3$ , and

asymmetric,  $\nu_8$ , stretchings in  $\sim 1415\text{cm}^{-1}$  and  $\sim 1570\text{cm}^{-1}$ , respectively. Energy of these two bands<sup>14</sup> may shift  $\pm 20\text{cm}^{-1}$ . This difference is very smaller in bidentate complexes than in ionic compounds and is larger in bridged complexes than in binuclear complexes.<sup>16</sup>

**Table 2. Infrared spectrum of acetate complex obtained in a KBr plate.**

Vibrational mode	Vibrational representation	Vibrating Species	Stretching Frequency
$A_1\nu_1$	$\nu\text{-CH}_3$	sym. str.	2936
$A_1\nu_2$	$\delta\text{-CH}_3$	sym. def.	1350
$A_1\nu_3$	$\nu\text{-CO}$	sym. str.	1447
$A_1\nu_4$	$\nu\text{-CC}$	stret.	950
$A_1\nu_5$	$\delta\text{-CO}_2$	sym. def.	658, 662(sh)
$A_1\nu_6$	$\rho\text{t-}$	torsion	---
$B_1\nu_7$	$\nu\text{-CH}$	antisym. def.	2980(sh)
$B_1\nu_8$	$\nu\text{-CO}$	antisym.def.	1587,1520(sh)
$B_1\nu_9$	$\delta\text{-CH}_3$	def.	1425
$B_1\nu_{10}$	$\delta_2\text{-CH}_3$	rock	1035
$B_1\nu_{11}$	$\delta_d\text{-CH}_3$	rock	530
$B_2\nu_{12}$	$\delta\text{-CH}$	antisym.def.	2980(sh)
$B_2\nu_{13}$	$\delta\text{-CH}_3$	def.	1430
$B_2\nu_{14}$	$\delta_t\text{-CH}_3$	rock	1050
$B_2\nu_{15}$	$\pi\text{-CO}_2$	out of plane	610(sh)

Monodentate acetates produce three bending  $\text{CO}_2$  in  $270\text{-}290\text{cm}^{-1}$  and one out of plane  $\pi(\text{CO}_2)$  about  $540\text{cm}^{-1}$ . These bands are absent in bridged complexes. while a decrease in number of these bands are observed for bidentate complexes<sup>12,13</sup>. A distinct band at about  $2500\text{-}2700\text{cm}^{-1}$  due to  $\nu(\text{OH})$  vibration is recognized for monodentate complexes.<sup>15,16</sup> Symmetric and asymmetric vibration of acetate ligands in  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$  depend on the charge and site of ion which also affect on the position of bending and stretching symmetric and asymmetric vibrations of  $\text{CO}_2$ . Asymmetric vibration of  $\text{CO}_2$  for this compound appears in  $1630\text{cm}^{-1}$ , which usually involves a weak shoulder about  $1580\text{cm}^{-1}$ . Weak band about  $360\text{cm}^{-1}$  and  $240\text{cm}^{-1}$

should be related to the stretching vibration of  $M-CO_2$  and out of plane vibration of  $M_3O$ , respectively.  $M_3O$  unit with a lone pair of electrons on oxygen is in the center of triangle with  $C_{3v}$  symmetry. Although this situation is probable for compounds with full d-orbitals, formation of  $d\pi-p\pi$  bonds for complexes of the type  $[Fe_3O(AcO)_6(H_2O)_3]^+$  results in a planar  $Fe_3O$  skeleton on the center of molecule with  $D_{3h}$  symmetry. Thus, it is expected that  $Fe_3O$  vibrations shift to higher energies for these compounds<sup>6</sup>. It should be noted that contribution of formation of  $\pi$ -bonds in center of triangle depends on the hardness of external ligands bonded to the triangle.

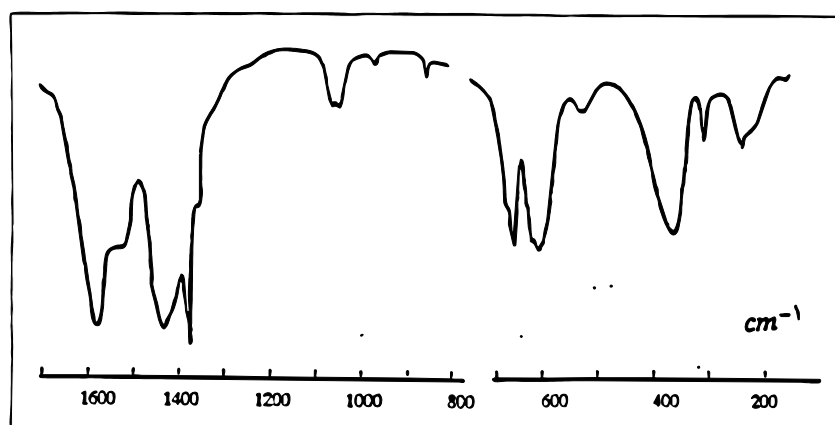


Figure 2. IR Spectrum of  $[Fe_3O(AcO)_6(H_2O)_3]^+$

Comparison of polarizability of M-L bonds determines hardness of ions and contribution of  $\pi(MO)$  bonds, which affects shifts in the position of spectral bands. Grifit believes that this shift is due to the localization of  $\pi$ -bonds on the metal and ligand atoms. Thus we think that M-O vibrations<sup>6</sup> in  $500-700\text{ cm}^{-1}$  are affected by changes in  $D_{3h}$  symmetry for the central triangle,  $M_3O$ , and  $C_{2v}$  symmetry for  $MO_4O'O''$  units around the triangle. Correlation between vibrational modes of these two symmetries is obtained in Table 3.

Considering  $\pi$ -resonance forms in central  $Fe_3O$  triangle, it was anticipated that the complex should not be completely centro symmetric. Thus a weak band corresponding to  $\nu(MM)$  was not observed at about  $100-250\text{ cm}^{-1}$ .

**Table 3. Correlation between  $\text{MO}_4\text{O}'\text{O}''$  ( $\text{C}_{2v}$ ) and  $\text{M}_3\text{O}(\text{D}_{3h})$  vibrational modes**

$\text{D}_{3h}$	$\nu_s(\text{A}'_1)$ (R)	$\pi(\text{A}''_2)$ (I.R)	$\nu_d(\text{E}')$ (I.R)		$\delta_d(\text{E}')$ (I.R)	
$\text{C}_{2v}$	$\nu(\text{A}_1)$ (I.R)	$\pi(\text{B}_1)$ (I.R)	$\nu_s(\text{A}_1)$ (I.R)	$\nu_a(\text{B}_2)$ (I.R)	$\delta_s(\text{A}_1)$ (I.R)	$\delta_a(\text{B}_2)$ (I.R)

**Table 4.  $\text{MO}_4\text{O}'\text{O}''$  ( $\text{C}_{2v}$ ) and  $\text{M}_3\text{O}(\text{D}_{3h})$  vibrations.**

**Vibration of  $\text{M}_3\text{O}(\text{D}_{3h})$  unit plane Vibration of the three  $\text{MO}_4\text{O}'\text{O}''$  ( $\text{C}_{2v}$ ) units With respect to the central unit**

Vibrational mode			Vibrational mode					
$E'$	$A''$	$A''_1$	$B_2$	$A_1$	$A_1$	$A_1$	$B_1$	$B_2$
(I.R)	(I.)	(R.)						
Kind of vibration								
$\nu_a(\text{MO})$	$\nu_s(\text{MO})$	$\nu_a(\text{MO})$	$\nu_d(\text{MO})$	$\nu_s(\text{MO})$	$\nu_a(\text{OMO})$	$\delta_d(\text{OMO})$	$\pi(\text{OMO})$	$\delta(\text{OMO})$
[ $\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3$ ]								
610	630	---	363	302	---	200	200	150

## Conclusion

If spectral bands of C-H and  $\text{CH}_3$  groups in Table 2 be ignored, except for susceptible spectral bands such as carboxylic and  $\text{M}_3\text{O}$  unit, we can summarize the following results.

One vibration is due to the bridging acetates and another are due to three water molecules bonded independently to the skeleton of the central metal triangle. For simplifying the description of vibrations, it is required to ignore hydrogen atoms of acetate ion and consider only water molecules bonded to the metals triangle.

Based on the preceding discussion and other findings<sup>17</sup>, it is expected that  $\text{M}_3\text{O}$  vibration should appear in  $500\text{-}700\text{ cm}^{-1}$  region. Because of appearance of the two vibrations of  $\delta(\text{COO})$  and  $\pi(\text{COO})$  in the case of coordinated acetates, this vibration

gives a complex structure in this region. In addition,  $\nu_{\text{asy}}$  vibration of  $\text{M}_3\text{O}$  should also appear in  $660\text{ cm}^{-1}$ . Where as, Grifit reported  $\nu_{\text{asy}}(\text{M}_3\text{O})$  vibration appears about  $614$  and  $621\text{ cm}^{-1}$ . For the three centered iron complex, this band appears around  $590\text{ cm}^{-1}$ , but vibration about  $614\text{ cm}^{-1}$  is not detectable. Another vibrational mode is due to  $\delta_{\text{asy}}(\text{M}_3\text{O})$ , which appears in  $250\text{-}350\text{ cm}^{-1}$ . This vibration appears in  $300\text{ cm}^{-1}$  in the three centered iron complex. Table 4 gives vibrations of  $\text{M}_3\text{O}$  unit, which is the result of combination of  $\text{M}_3\text{O}$  ( $\text{D}_{3\text{h}}$ ) vibration with  $\text{MO}_4\text{O}'\text{O}''$  ( $\text{C}_{2\text{v}}$ ) vibrations of the three side units.

According to our abinitio calculations performed on various methods such as LSDF/6-31G\* and LSDF/6-31G\*\* on  $\text{M}_3\text{O}$  skeleton with six bridged acetate ligands bonded to iron atoms in Helium atmosphere, all chemical bonds and related angles have been determined (Table 1). For bridging acetate, the value of  $124.241$  obtained, which agrees with Negro angle<sup>8</sup> well. This value confirms  $\text{C}_{2\text{v}}$  symmetry for the plane formed by the bridging acetate ligands.

Further more, our abinitio calculations indicated that the cyclic acetate systems are relatively distorted to each other. This finding is in accord with the previous results which firmly established that the metal ions in the oxo-centered units are antiferromagnetically coupled<sup>2-6</sup>. But, it is noteworthy that all recent measurements indicate that the three magnetic coupling constants are not equal.

Infrared vibrations of  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]$  are generally similar to  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$ , but bands at  $200\text{-}350\text{ cm}^{-1}$  in terminal side of the spectrum are wider and involve more shoulders. The width of these bands should be due to differences in  $\text{Fe}^{+2}\text{-O}$  and  $\text{Fe}^{+3}\text{-O}$  vibrations.

Study of charge transfer in a molecule gives some information on the effects of surrounding and extent of localization of valence electrons. Several findings showed that in some changed complexes of the type  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]$ , the two  $\text{Fe}_3\text{O}$  units surround a solvent molecule in a sandwich form. Thus our method in preparation of



$[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$  is suitable for complexes which their primary salt, as  $\text{FeC}_3$ , has electron acceptor behavior.

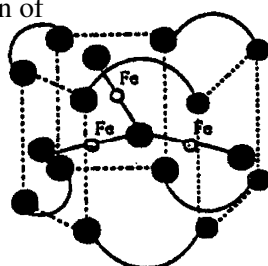
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Infrared Spectrum of

$[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$

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The complex  $[\text{Fe}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]^+$  was prepared.

The structures of complex were calculated. IR spectrum of this complex was discussed considering  $D_{3h}$  symmetry for the central  $\text{Fe}_3\text{O}$  unit and  $C_{2v}$  symmetry for  $\text{FeO}_4\text{O}''$  side units.

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