A New Method of Preparation, Abinitio Calculation and Description of Infrared Spectrum of $[Fe_3O(AcO)_6(H_2O)_3]^+$

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Abstract

The complex $[Fe_3O(AcO)_6(H_2O)_3]^+$ was prepared by treating 1, 3, 5-trimethy l-2, 4, 6-trioxane with $FeCl_3$. $6H_2O$ 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 Fe_3O unit, and C_{2v} symmetry for trans- Fe O'O"O_4 - units chelated on iron ions around the three centred nuclei, are proposed. Combination vibration of these two units resulted in explanation and charactrization 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 pastfew decades.[1-3] Among them, complexes of the type $[M_3O(AcO)_6(H_2O)_3]X.nH_2O$,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.[4] Synthesis of acidic and dianionic salts such as alkali hydrogen diacetate is reported by the reaction of alkali metals with 1, 3, 5-trimethy l-2, 4, 6-trioxane as the starting material.[5] Now a new simple method is proposed for one pot preparation of chlorinated $[Fe_3O(AcO)_6(H_2O)_3]^+$ by treating $FeCl_3$. $6H_2O$. with the above methylated trioxane. Then, the results on the charactrization and interpretation of IR spectrum of this compound areintroduced in a new point of view.

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Experimental Section

One hunred ml of freshly distilled 1, 3, 5-trimethy l-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) $FeCl_3$. $6H_2O$ 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 $[Fe_3O(AcO)_6(H_2O)_3]Cl$ was obtained. (6.7 g) with 65% yield. Infrared spectrum of $[Fe_3O(AcO)_6(H_2O)_3]^+$ 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 varius systems namely UHF/6-31 $G^{**}$and LSDF/6-31 G^{**}. 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_3O atoms formed an triangle array with 120° angle and D_{3h} 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 $FeO'O''O_4$. Thus the angle values O_1-Fe-O_2(88.815deg.) and O_2-Fe-O_3(91,319 deg.) cofirm a C_{2v} skeleton for $MO_1O_2O_3O_4$ plain. The planes of the three H_2O 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.[10] Clearly, all the three centred oxo-carboxylates show similar structure, but differ in the kind ofnonacetate ligands. Infrared and Raman vibrations of $[Fe_3O(AcO)_6(H_2O)_3]^+$ are discussed based on

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vibrations of units , which interact with each other and finally combine with vibrations of Fe_3O as central triange skeleton.

Table 1. Abinitio calculation for selected distances (Å) and Angles. for complex $[Fe_3O(AcO)_6(H_2O)_3]Cl$.

Mean value	LSDF/6-31G**	UHF/6-31G**	Band/Angel
O-C-O(deg)	123.582	124.901	124.241(deg)
Fe_1-O' -Fe_1(deg)	120	120	120(deg)
O'-Fe_1-O_1(deg)	96.360	94.512	95.371(deg)
	96.361	94.215	
O_1-Fe_1-O_2(deg)	88.809	88.801	88.815(deg)
O_2-Fe_1-O_3(deg)	91.081	91.198	91.139(deg)
Fe_1-O_1-C_1(deg)	132.107	130.100	131.136(deg)
Fe_1-O' (Å)	1.8230	1.8520	1.8375 (Å)
Fe_1-O_1(Å)	1.9893	1.9625	1.9759 (Å)
C_1-O_1(Å)	1.2359	1.2097	1.2228 (Å)
Fe_1-O" (Å)	1.8021	1.8853	1.8437 (Å)
Fe_1-Fe2(Å)	3.2881	3.2790	3.2836 (Å)

Grifit[6] pointed out, vibrational spectrum of molecule is the result of interaction of central Fe_3O unit with D_{3h} symmetry and its surrounding with D_{4h} symmetry. Jhonson7believes that final vibration of molecule is the result of vibrations of FeO_4 side units with C_{4v} symmetry and central Fe_3O triangle with D_{3h} symmetry. According to the general structure of molecule in Fig. 1, FeO_4 side units and Fe_3O 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_4 units with C_{2v} local symmetry with vibrations of central Fe_3O skeleton with D_{3h} local symmetry. This explanation is in accord with findings of Negro[8], in which the angle of $124^\circ - 125^\circ$ calculated for acetate bridges with C_{2v} symmetry. Grigorev[9] believes that vibrations in this angle depends on the kind of metal, increase in energy of ν_3 vibration, and decrease in energy of ν_8 vibration (Table 2). Considering Fig. 1.The atoms O_1, O_2, O_3 and O_4 are

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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[2,4,10-12].

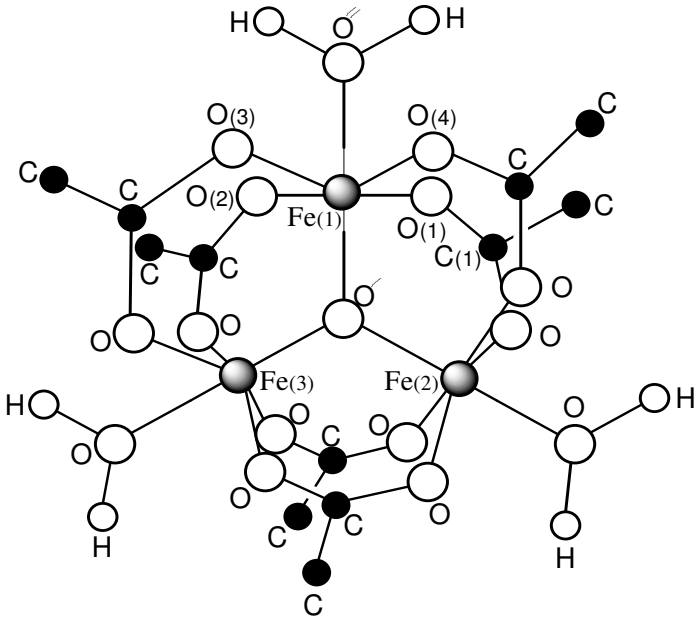

Figure 1. General Structure of [Hexa-μ-acetato-μ-trioxotriiron(III)].

According to the above discussions, $FeO'O''O_4$ unit should occupy a position with C_{2v} symmetry. Thererfore, fifteen vibrational modes are proposed for this part of molecule[13]. 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 $[Fe_3O(AcO)_6(H_2O)_3]^+$. Most important vibrations of this complex are due to CO, 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 $MO_4O'O''$ (C_{2v})and $M_3O(D_{3h})$ 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[14]. According to IR spectrum of molecul in Fig. 2, most important vibrations in acetate are symmetric, ν_3, and

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asymmetric, ν_8, stretchings in ~1415cm^{-1} and ~1570 cm^{-1}, respectively. Energy of these two bands[14] may shift ±20 cm^{-1}.This difference is very smaller in bidentate complexes than in ionic compounds and is larger in bridged complexes than in binuclear complexes.[16]

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

Vibrational mode	Vibrational representation	Vibrating Species	Stretching Frequency
$A_1\nu_1$	ν-CH_3	sym. str.	2936
$A_1\nu_2$	δ-CH_3	sym. def.	1350
$A_1\nu_3$	ν-CO	sym. str.	1447
$A_1\nu_4$	ν-CC	stret.	950
$A_1\nu_5$	δ-CO_2	sym. def.	658, 662(sh)
$A_1\nu_6$	ρt-	torsion	---
$B_1\nu_7$	ν-CH	antisym. def.	2980(sh)
$B_1\nu_8$	ν-CO	antisym.def.	1587,1520(sh)
$B_1\nu_9$	δ-CH_3	def.	1425
$B_1\nu_{10}$	δ2-CH_3	rock	1035
$B_1\nu_{11}$	δd-CH_3	rock	530
$B_2\nu_{12}$	δ-CH	antisym.def.	2980(sh)
$B_2\nu_{13}$	δ-CH_3	def.	1430
$B_2\nu_{14}$	δt-CH_3	rock	1050
$B_2\nu_{15}$	π-CO_2	out of plane	610(sh)

Monodentate acetates produce three bending CO_2 in 270-290 cm^{-1} and one out of plane π (CO_2) about 540 cm^{-1}. These bands are absent in bridged complexes. while a decrease in number of these bands are observed for bidentate complexes[12,13]. A distinct band at about 2500-2700 cm^{-1} due to ν(OH) vibration is recognized for monodentate complexes.[15,16] Symmetric and asymmetric vibration of acetate ligands in $[Fe_3O(AcO)_6(H_2O)_3]^+$ depend on the charge and site of ion which also affect on the position of bending and stretching symmetric and asymmetric vibrations of CO_2. Asymmetric vibration of CO_2 for this compound appears in 1630 cm^{-1}, which usually involves a weak shoulder about 1580 cm^{-1}. Weak band about 360 cm^{-1} and 240 cm^{-1}

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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 dπ-pπ bonds for complexes of the type $[Fe_3O(AcO)_6(H_2O)_3]^+$ results in a planar Fe_3O skeletonon the center of molecule with D_{3h} symmetry. Thus, it is expected that Fe_3O vibrations shift to higher energies for these compounds[6]. It should be noted that contribution of formation of π-bonds in center of triangle depends on the hardness of external ligands bonded to the triangle.

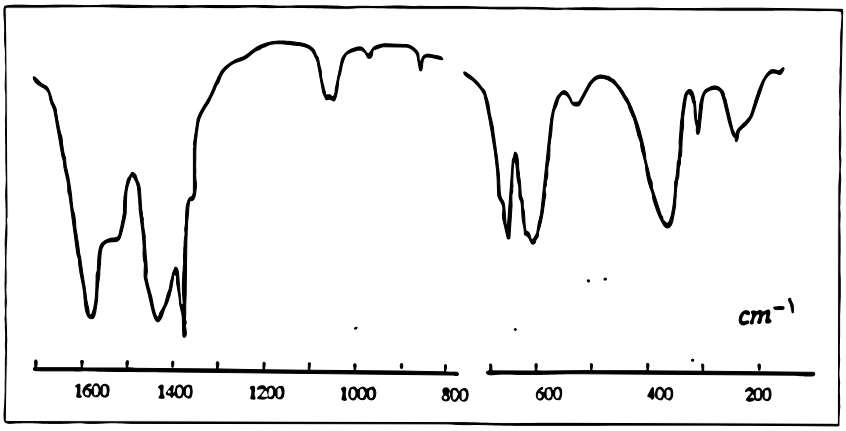

Figure 2. IR Spectrum of $[Fe_3O(AcO)_6(H_2O)_3]^+$

Comparison of polarizability of M-L bonds determines hardness of ions and contribution of π(MO) bonds, which affects shifts in the position of spectral bands.Grifit believes that this shift is due to the localization of π-bonds on the metal and ligand atoms. Thus we think that M-O vibrations[6] in 500-700 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 π-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 ν(MM) was not observed at about 100-250 cm^{-1}.

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Table 3. Correlation between $MO_4O'O''$ (C_{2v}) and M3O(D_{3h}) vibrational modes

D_{3h}	$\nu_s(A'_1)$ (R)	$\pi(A''_2)$ (I.R)	$\nu_d(E')$ (I.R)		$\delta_d(E')$ (I.R)	
C_{2v}	$\nu(A_1)$	$\pi(B_1)$	$\nu_s(A_1)$	$\nu_a(B_2)$	$\delta_s(A_1)$	$\delta_a(B_2)$
	(I.R)	I.R)	(I.R)	(I.R)	(I.R)	(I.R)

Table 4. $MO_4O'O''$ (C_{2v}) and $M_3O(D_{3h})$ vibrations.
Vibration of $M_3O(D_{3h})$ unit plane Vibration of the three $MO_4O'O''$ (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	B1	B_2
(I.R)	(I.)	(R.)						
Kind of vibration								
ν_a(MO)	ν_s(MO)	ν_a(MO)	ν_d(MO)	ν_s(MO)	ν_a(OMO)	δ_d(OMO)	π(OMO)	δ(OMO)
$[Fe_3O(AcO)_6(H_2O)_3]$								
610	630	---	363	302	---	200	200	150

Conclusion

If spectral bands of C-H and CH_3 groups in Table 2 be ignored, except for susceptible spectral bands such as carboxylic and M_3O 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[17], it is expected that M_3O vibration should appear in 500-700 cm^{-1} region. Because of appearance of the two vibrations of δ(COO) and π(COO) in the case of coordinated acetates, this vibration

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gives a complex structure in this region. In addition, ν_{asy} vibration of M_3O should also appear in 660 cm^{-1}. Where as, Grifit reported $\nu_{asy}(M_3O)$ vibrationappears about 614 and 621 cm^{-1}. For the three centered iron complex, this band appears around 590 cm^{-1}, but vibration about 614 cm^{-1} is not detectable. Another vibrational mode is due to $\delta_{asy}(M_3O)$, which appears in 250-350 cm^{-1}.This vibrationappears in 300 cm^{-1} in the three centered iron complex. Table 4 gives vibrations of M_3O unit, which is the result of combination of M_3O (D_{3h}) vibration with $MO_4O'O''$ (C_{2v}) 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 M_3O skeleton with six bridged acetate ligands bonded to iron atoms in Helium atomosphere, all chemical bonds and related angles have been determined (Table 1). For bridging acetate, the value of 124.241obtained, which agrees with Negro angle[8] well. This value confirms C_{2v} 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[2-6]. But, it is noteworthy that all recent measurements indicate that the three magnetic coupling constants are not equal.

Infrared vibrations of $[Fe_3O(AcO)_6(H_2O)_3]$ are generally similar to $[Fe_3O(AcO)_6(H_2O)_3]^+$, but bands at 200-350 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 Fe^{+2}-O and Fe^{+3}-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 $[Fe_3O(AcO)_6(H_2O)_3]$, the two Fe_3O units surround a solvent molecule in a sandwich form. Thus our method inpreparation of

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$[Fe_3O(AcO)_6(H_2O)_3]^+$ is suitable for complexes which their primary salt, as FeC_3, has electron acceptor behavior.

A New Method of Preparation abinitio calculatio and Description of Infrared Spectrum of $[Fe_3O(AcO)_6(H_2O)_3]^+$

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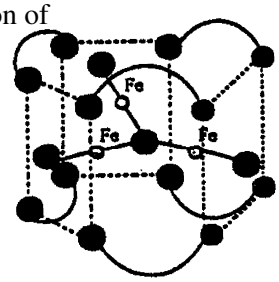
R. Tayebee



The complex $[Fe_3O(AcO)_6(H_2O)_3]^+$ was prepared.

The structures of complex were calculated. IR spectrum of this complex was discussed considering D_{3h}summetry for the central Fe_3O unit and C_{2v} symmetry for $FeO_4O'O''$side units.

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