

**Low Spin Iron (III) - Triethanolamine Complex
Characterization and Physico -Chemical Studies**

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Low spin iron (III)-triethanolamine complex, $[\text{Fe}(\text{TEA})\text{Cl}_2]\text{Cl}$, was prepared and characterized. The IR spectra proved that the coordination occurs via oxygen and nitrogen atoms of the triethanolamine. The nujol mull electronic absorption spectra and the room temperature magnetic moment value indicated the O_h geometry with the possibility of the Fe-Fe interaction. The molecular structure of the complex is examined by chem. 3D program in a personal computer at Chemistry Department, Faculty of Science, Alexandria University. Thermo-gravimetric measurements and differential thermal analysis were performed. The thermodynamic parameters of the decomposition steps are calculated. The electrical conductivity pattern is examined. The data point to semi-conducting trend with criterion for applying the hopping for the conduction.

Keywords: Triethanolamine; iron (III), Low spin complex.

Introduction

Metal ethanolamine complexes were the subjects of many studies in the recent decade. The origin of these investigations arose from the importance of their technical applications in different fields [1-8]. In our laboratory, extensive studies on the structural chemistry of mono-, di-, and triethanolamine complexes were reported [9-20]. The study of the interaction between iron (III) ion and mono-, di- and triethanolamine were studied mainly in solutions. This paper will study the reaction between iron (III) and triethanolamine, which can be considered as biomimetic tripodal ligand. This may help in understanding the mechanism of the metalloproteins and for the developing of new low molecular weight biomimetic molecules.

Experimental

Instrumentation C, H, N, Cl and Fe determinations were performed by elemental analysis at the Central Laboratory, Faculty of Science, Alexandria University, Alexandria, Egypt. The ionizable chloride was determined gravimetrically as AgCl.

Infra red spectra were recorded as KBr disk using Perkin Elmer spectrophotometer model 1430 covering range of $200\text{-}4000\text{ cm}^{-1}$.

The electronic absorption spectral data were recorded by Perkin Elmer spectrophotometer model 4B covering range of 190 – 900 nm. The spectrum was measured in nujol mull, following the method described by Lee *et al* [21].

Room-temperature magnetic susceptibility of well ground solid sample was measured by using an Evan balance. The measurements were calibrated against a Hg[Co(SCN)₄] standard [22].

Thermo-gravimetric measurements and differential thermal analysis were performed on a Du pont 9900 computerized thermal analyzer. The heating rate was 10 degree/min. A 60 mg sample was placed in a platinum crucible. Dry nitrogen was flowed over the sample at a 10 cc/min rate and a chamber cooling water flow rate was 10 l/h. The electrical conductivity measurement were done in the temperature range 294-750 K. The complex was prepared in the form of a tablet at a pressure of 4 ton /cm². The tablet was of an area 2.54 cm² and 0.12 cm thickness. The sample was hold between two Cu electrodes with silver paste in between and then inserted with the holder vertically into cylindrical electric furnace. Both ends of the furnace were closed off to reduce drafts. The potential drop across the heater was varied gradually through variac transformer to produce slow rate of increasing temperature to get accurate temperature measurements.

The circuit used to measure the electric conductivity consists of D.C. regulated power supply Heat Kit (0.400 Volts), Keith multi-meter for measuring current with sensitivity up to 10⁻¹⁵ ampere. The temperature of the sample was measured within ± 0.1 degree by means of copper-constant thermocouple. The conductivity was obtained in the case of cooling using the general formula: $\sigma = I d / V_c a$ where, I is the current in ampere, V_c is the potential drop across the sample of cross section area “a” and thickness “d”.

Synthesis of the low spin iron (III) - triethanolamine complex

A 0.15 gm (~ 1.0 mmol) of triethanolamine, TEA, was mixed with 30 ml of ethanol. When a 0.27 gm (1 mmol) of iron (III) chloride hexahydrate was added to the solution, it becomes brown solution. After an hour of stirring and slow evaporation of the solution for 5 days brown precipitate is obtained. The complex was filtered and washed several times by EtOH then dried in a desiccator over anhydrous CaCl₂.

Analytical Results: [Fe(TEA)Cl₂]Cl (FeC₆H₁₅Cl₃NO₃) (F.wt.= 311.39).

Calculated: C, 23.14; H, 4.86; Cl, 34.16; Fe, 17.93; N, 4.50 %

Found: C, 23.12; H, 4.82; Cl, 34.18; Fe, 17.91; N, 4.52 %

[λ_{\max} (nujol) 352.0, 550.0 nm], μ_{eff} : 2.03 BM.

Results and discussions

[Fe(TEA)Cl₂]Cl was synthesized by using ferric chloride and TEA as tripodal tetra dentate ligand. The magnetic moment of the complex at room temperature, 2.03 BM., is comparable to the low spin iron (III) systems. The magnetic moment of the latter systems were to be decreased with decreasing temperature. This is characteristic configuration (²T_{2g} ground state) [23]. The lower value of the recorded magnetic moment value than that of the low spin iron (III) complexes, 2.2 BM., may be attributed to presence of Fe-Fe interaction. The electronic absorption spectra gave the spectra of the low spin O_h iron (III) complexes where two spectral bands are observed at 352.0 and 550.0 nm. The bands are due to L→M charge transfer transitions from both of Cl and OH groups of the TEA molecules. The IR spectra of the complex indicated that the coordination occurs through nitrogen and oxygen sites. The stretching vibration bands due to $\nu_{\text{Fe-N}}$ and $\nu_{\text{Fe-O}}$ appeared at 449 and 330 cm⁻¹, respectively. The peak at 294 cm⁻¹ indicated the $\nu_{\text{Fe-Cl}}$ mode of vibration. It seems that the two coordinated Cl atoms may interact positively with two OH groups of the TEA resulting in intermolecular hydrogen bonds. This facilitate the coordination bonds of the two Cl atoms and two of the OH groups of the ligand resulting in an increasing L→ M CT. Thus, the third OH group of the ligand bind weakly with Fe because of the steric hindered of the whole molecule, and may be easily broken and the Fe-Fe bond will be formed instead resulting in lower spin complex.

When the molecular structure of the [Fe(TEA)Cl₂]Cl complex is examined by chem. 3D program in a personal computer at Chemistry Department, Faculty of Science, Alexandria University, interesting dater are observed. Selected bon lengths (Å) and angles (°) for the complex are shown in Table I, and the suggested ORTEP drawing of the cation is shown in Figure I.

Table I: Selected bond lengths (Å) and angles (°) for [Fe(TEA)Cl₂]Cl complex

Fe(1)-N(1)	1.861	Fe(1)-O(3)	1.822
Fe(1)-O(1)	1.823	Fe(1)-Cl(1)	2.184
Fe(1)-O(2)	1.828	Fe(1)-Cl(2)	2.180
O(1)Fe(1)N(1)	88.586	Cl(2)Fe(1)O(1)	89.030
O(2)Fe(1)N(1)	84.674	O(3)Fe(1)O(2)	84.978
O(3)Fe(1)N(1)	91.462	Cl(1)Fe(1)O(2)	86.243
Cl(1)Fe(1)N(1)	169.612	Cl(2)Fe(1)O(2)	177.589
Cl(2)Fe(1)N(1)	93.420	Cl(1)Fe(1)O(3)	92.754
O(2)Fe(1)O(1)	89.449	Cl(2)Fe(1)O(3)	96.559
O(3)Fe(1)O(1)	174.398	Cl(2)Fe(1)Cl(1)	95.517
Cl(1)Fe(1)O(1)	86.295		

From Table I, the Fe-N bond was 1.861 Å and two Fe-Cl bond lengths are observed 2.184 and 2.180 Å. The difference may be due to the different of the *trans* groups of the two chlorides. Two closed Fe-O bonds are observed, 1.822 and 1.823 Å, these values corresponding to the bonds between Fe and the two OH groups, which are *trans* to each other. One Fe-O bond length was found to be 1.828 Å, the difference may be due to the *trans* effect of the *trans* Cl atom.

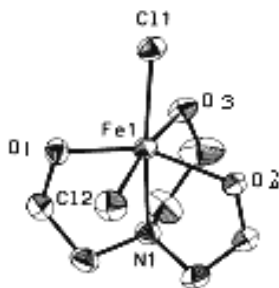


Figure I: The suggested ORTEP drawing of $[\text{Fe}(\text{TEA})\text{Cl}_2]^+$

Electrical conductivity

The temperature dependence of the electrical conductivity of the iron (III) - triethanolamine complex obeys the following equation [24]:

$$\sigma = \sigma_0 \exp \frac{-\Delta E}{KT}$$

Where σ and ΔE are the specific conductivity and the activation energy, respectively, σ_0 is a pre-exponential term, K Boltzmann constant. The conductivity curve of the studied complex, Figure II, showed two temperature dependence regions: A and B. The transition temperature is 344.9 K. The $\log \sigma_0$ values are -14.4 and -15.7 $\text{ohm}^{-1}\text{cm}^{-1}$ for regions A and B, respectively. The activation energy values for the conduction are 0.078 and 0.025 eV for regions A and B, respectively. The data point to the semi-conducting trend.

The mobility, μ , of the studied complex is calculated based on the equation: $c = eN_0\mu$, Where N_0 is the number of current carriers, $N_0 = 10^{21}$. The values of μ are found to be within the range $10^{-9} - 10^{-13} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The fact that these values are much smaller than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ can be used as a criterion for applying the hopping for the conduction. Therefore the charge carrier passes to another molecule over the top of barrier via an excited state [25].

Thermal analysis

The DTA data of the prepared iron (III) triethanolamine complex are given in Table II. The complex gave three DTA peaks. The first peak found at 359 K, with activation energy E_a of 39.4 kJ/mol and order, n , of 0.98. This peak may be due to rearrangement process or

dissociation of the hydrogen bonds affecting the packing of the molecules in the tablet. The second and third peaks at 510 and 666 K, with activation energies of 829.6 and 744.4 kJ/mol and orders of 1.2 and 1.1, respectively, may be due to decomposition of the complex and formation of Fe₂O₃ as a final product.

Table II: The thermal parameters of the iron (III) triethanolamine complex.

Complex	T _m K	E _a KJ mol ⁻¹	N	α _m	ΔS [‡] kJ mol ⁻¹ K ⁻¹	Z s ⁻¹
[Fe(TEA)Cl ₂]Cl	359.	39.4	0.98	0.636	-0.240	2.28
	510	829.6	1.2	0.411	-0.217	48.4
	666	744.4	1.1	0.411	-0.224	28.0

The change of entropy, ΔS[‡], values are nearly of the same magnitude and lie within the range of -0.217 to -0.240 kJ mol⁻¹ K⁻¹. So the transition states of the decomposition steps are more ordered, i.e. in a less random molecular configuration than the reacting complex. The fraction appeared in the calculated order of the thermal reactions, n, also confirmed that the thermal reaction proceeded in complicated mechanisms. The calculated values of the collision number, Z, showed a direct relation to E_a.

The peak temperature, T_m, at which the peak maximum or minimum occurs, defines the position of the peak. The value of the decomposed substance fraction, α_m, at maximum development of the reaction was calculated from the following equation [26]:

$$(1 - \alpha_m) = n^{\frac{1}{n-1}}$$

The entropy of activation, ΔS[‡] is calculated from the following equation [27]:

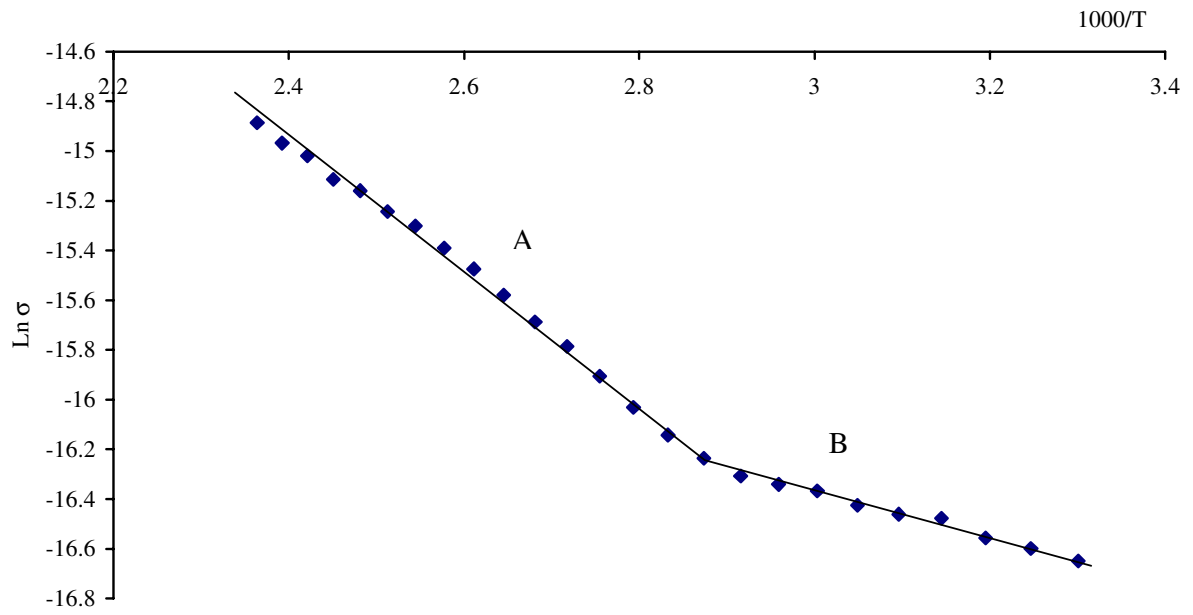
$$Z = \frac{KT_m}{n} \exp\left[\frac{\Delta S^{\ddagger}}{R}\right]$$

The values of Z were obtained by Horowitz Metzger equation [28]:

$$Z = \frac{E_a}{RT_m} \phi \exp\left[\frac{E}{RT_m^2}\right]$$

Where R represent molar gas constant, φ is the heating rate (Ks⁻¹), K is the Boltzmann constant and h is the Planck's constant.

Figure II: Electrical conductivity of the $[\text{Fe}(\text{TEA})\text{Cl}_2]\text{Cl}$ complex.



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