

Preparation, Characterization and Molecular Models of the Complexes of Triethylenetetramine with Cr(III) and Fe(III)

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Abstract : Triethylenetetramine was reacted with Cr(III) and Fe(III) in EtOH medium. In each case solid crystalline products were precipitated out. The complexes were formulated by comparing C H N and metal analysis data. Uv-visible and IR spectra of the complexes have been discussed. The molecular model calculation suggests the *trans* geometry of the complexes.

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Introduction

The chemistry of metal complexes is of important biological significance. Understanding the nature of bonding, structure and reactivity of coordination compounds is a challenge to the chemists from nineteenth century. Many of the biologically important compounds such as hemoglobin, myoglobin, chlorophyll, metallo-proteins etc. are by and large coordination compounds and are associated with the chemistry of life.

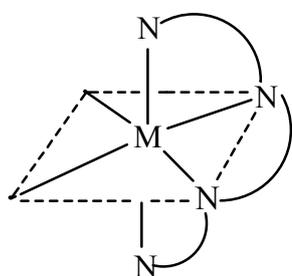
Triethylenetetramine (trien) is a quadridentate ligand having four amino groups, two of them are primary amino and the other two are secondary amino groups; so, it can donate 4N lone pairs of electrons to metal ions. Metal complexes of trien exhibit three possible geometric isomers, designated as *cis- α* , *cis- β* and *trans-*, and may be shown as below,

Both the *cis* isomers have an asymmetric arrangement of the ligand moiety around the metal atom but the *trans* isomer appears to have two plane of symmetry excluding the asymmetry arising from secondary >NH group. Coordination complexes of trien, of different geometry and macrocyclic complexes have been reported [1-8]. In this paper we report the preparation and characterization of triethylenetetramine complexes with trivalent metals Cr(III) and Fe(III). The molecular geometry of the complexes has been suggested from the steric energy calculation of the molecular models.

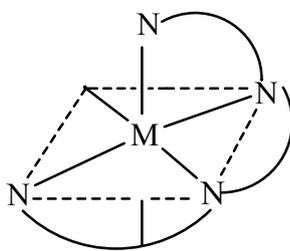
Experimental

Chemicals and Equipments

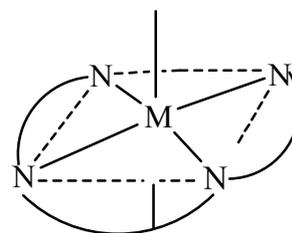
Analar grade (AR) chemicals and ligand were used in the preparation and analytical work (Aldrich, E. Merck, and BDH). Micro analytical



cis- α



cis- β



trans

data for C, H, N were obtained from Tohoku University, Japan. Metal contents were determined by volumetric titration [9]. IR spectra of the complexes were recorded on a Shimadzu Infrared Spectrophotometer in the range 4000-400 cm^{-1} in the form of KBr pellets and that of the ligand as thin film between NaCl cells. Electronic Spectra were recorded on Shimadzu UV-160A UV-Visible spectrophotometer, between 200-1100 nm using nujol mull technique. Melting points were measured in a heating device, MEL-TEMP(II), with a FLUKE51KJ thermometer, USA, in the temperature range 40-700 $^{\circ}\text{C}$. Molecular modeling calculations were done using the softwares Gaussian 03 and Gauss View 03 of Gaussian Inc, USA

Synthesis and formulations:

Cr(III) triene complex $[\text{Cr}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_3].6\text{H}_2\text{O}$: 0.62 g of $\text{CrCl}_3.6\text{H}_2\text{O}$ was dissolved in 10 mL EtOH and filtered. This solution was added to the ligand solution (0.56 g triene in 10 mL EtOH) slowly. The colour of the solution turned in to violet and it was kept for crystallization at room temperature. Violet solid product was obtained after overnight staying. The product was separated by filtration washed with cold EtOH and dried over silica gel. The compound is stable in air and light. It is sparingly soluble in hot water and insoluble in common organic solvents like ethanol, methanol, acetone and carbon tetrachloride.

	%C	%H	%N	%Cr
<i>Calc</i>	17.45	7.31	13.57	12.59
<i>Found</i>	17.94	6.82	12.92	13.23

m.p. : decomposes above 360 $^{\circ}\text{C}$;
yield : ~ 60 % (on metal content)

IR bands (cm^{-1}) : 3795 (sh), 3440 (s,b), 2965 (sh), 1634 (m), 1601(sh), 1591(m), 1432 (m), 1373 (m), 1114 (m), 1033 (m), 663(m)

Fe(III) triene complex $[\text{Fe}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NO}_3)_3].6\text{H}_2\text{O}$: Alcoholic solutions of $\text{Fe}(\text{NO}_3)_3.9\text{H}_2\text{O}$ (2.3 g in 10 mL EtOH) and the ligand, triene (0.61 g in 10 mL EtOH) were prepared separately. After filtration the metal salt solution was added to the ligand solution slowly and kept for crystallization at room temperature. Redish yellow solid product was obtained after two days. The product was separated by filtration washed with cold EtOH and dried over silica gel. The compound is stable in air and light. It is sparingly soluble in hot water and insoluble in common organic solvents like ethanol, methanol, acetone and carbon tetrachloride.

	%C	%H	%N	%Fe
<i>Calc</i>	14.52	6.08	19.78	11.26
<i>Found</i>	13.92	5.86	19.77	12.72

m.p. : decomposition starts at 187 $^{\circ}\text{C}$;
yield : ~ 63 % (on metal content)

IR bands (cm^{-1}) : 3790 (sh), 3455 (s), 3025 (s), 1601 (sh), 1575 (m), 1397 (sh), 1296 (m), 1159 (m), 1123 (m), 1095 1065, 1018

Results and Discussion

The empirical formulae of the complexes were determined by comparing the analytical data for C, H, N and metal with the calculated values. The good agreement between calculated and experimental values indicates that the compounds are fairly pure. The low decomposition temperatures of the complexes are indicative of their covalent nature.

The IR spectra of these compounds were studied in detail. Tentative assignments of the ir bands are shown in Table 1. The bands which are important for understanding metal ligand bonding have been assigned on the basis of standard references [10-12] and by comparing with the absorption bands of the ligand and other related compounds.

Table-1: Tentative assignment of important IR bands.

Compounds	ν (OH), ν (H_2O) ν (NH) cm^{-1}	ν (CH) cm^{-1}	NO_3^- group cm^{-1}	δ (N-H) of NH_2 gr. cm^{-1}	ν (CH_2) cm^{-1}	ν (CN) cm^{-1}
Triethylenetetramine	3450-3200	2915		1615	1452	1123
<u>A</u> $[\text{Cr}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_3].6\text{H}_2\text{O}$	3795-3440	2965		1601	1442	1114
<u>B</u> $[\text{Fe}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NO}_3)_3].6\text{H}_2\text{O}$	3790-3455	3025	1397	1634	1450	1159

All the complexes show strong and broad absorption for OH, H₂O and NH stretching in the 3545-3190 cm⁻¹ regions. CH absorption bands are obtained at 2940-2915 cm⁻¹ ranges. Absorptions for NH bending mode of vibrations appear in the 1645-1601 cm⁻¹ region. Typical stretching mode for CH₂ group appears in the range 1452-1432 cm⁻¹ for all the complexes. All the compounds show C-N (of triene) stretching vibrations slightly above 1100 cm⁻¹.

The uv-visible spectra of the ligand and the complexes were investigated. The absorption bands are listed in Table 2. The assignments of the absorption bands have been made on the basis of standard books [13,14]. Triethylenetetramine showed absorption bands at 302, and 235 nm, of

which the intense band at 235 nm is due to $n \rightarrow \sigma^*$ transition of the nitrogen lone pair to the antibonding orbital of C-N bond. The other band could not be identified (Figure 1). The absorption bands of the complexes in the 200–350 nm range are identical to each other which demonstrate that the organic moiety of the complexes have the same structure. After complexation the nitrogen lone pairs of the ligand moiety are no longer non bonding electrons. The three bands appeared for both the compounds in the 200-350 nm range may be due to $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand, counter ion and H₂O molecule in the compounds. All the complexes absorb due to CT transitions at A 400 & B 389, nm and due to d-d transitions at A 546, & B 495, nm respectively.

Table-2: Absorption bands of Triethylenetetramine and the metal complexes:

Compounds	Absorption Bands				
	d-d nm	CT nm	$n \rightarrow \pi^*$ nm	$\pi \rightarrow \pi^*$ nm	$n \rightarrow \sigma^*$ nm
Triethylenetetramine					235
<u>A</u> [Cr(C ₆ H ₁₈ N ₄)Cl ₃]. 6H ₂ O	546	400	340	299	245
<u>B</u> [Fe(C ₆ H ₁₈ N ₄)(NO ₃) ₃]. 6H ₂ O	495	389	324	298	248

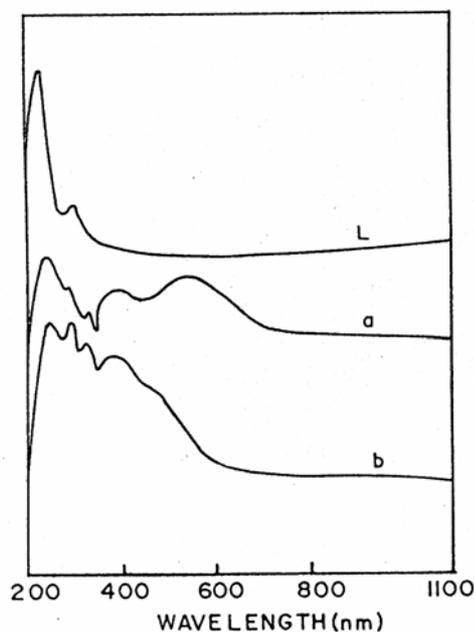


Figure 1 : Comparison between the uv-visible spectra of the ligand and the complexes (a) Cr(III)-triene complex and (b) Fe(III)-triene complex

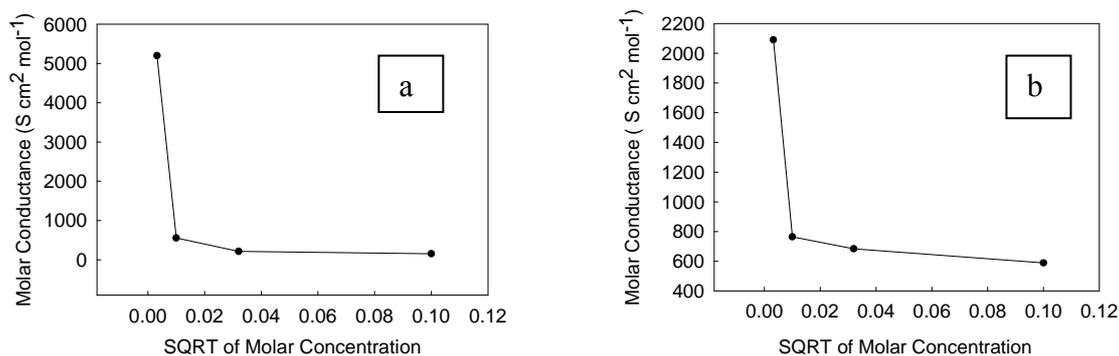


Figure 2 : Molar conductance vs SQRT of molar concentration for a) $[\text{Cr}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_3] \cdot 6\text{H}_2\text{O}$ and b) $[\text{Fe}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NO}_3)_3] \cdot 6\text{H}_2\text{O}$

The conductance in dilute aqueous solutions of the complexes (taking the formula weight as molar mass) was measured at different concentration (1×10^{-2} to 1×10^{-5} M). The molar conductance values of these compounds as shown in Figure 2, increase rapidly with dilution. This fact further supports that the bonding in the complexes is mainly of covalent nature and that they behave like weak electrolytes.

Molecular modeling of these compounds were done by using Gaussian software. The structures of the compounds have been optimized in the ground state on the basis of Density Functional Theory (DFT) using the method B3LYP and the basis set SDD [15]. The steric energies of the complexes for three different possible geometries (*cis- α* , *cis- β* and *trans-*) have been calculated. The optimized structures of the compounds are shown in Figure 3a & 3b. For simplicity hydrogen atoms and lone pairs are omitted from the figure. The bond lengths and

bond angles within the coordination sphere of the optimized structure are listed in Table 3.

From the calculated data it is evident that the complexes undergo Jahn-Teller distortion and have distorted octahedral structures. The compounds are distorted in bond lengths as well as bond angles. In Fe-complex the axial bonds are relatively shorter than the equatorial bonds which indicates that the complex suffers distortion in the equatorial plane, whereas, in the Cr-complex the axial bonds are longer than the equatorial bonds. This axial distortion may be due to higher electro negativity of the Cl atoms at the axial position of the Cr-complex. In both the complexes the axial bonds are not in the same line. The bending is higher in the Fe-complex ($\text{NO}_3\text{-Fe-NO}_3$, 165.683°) than in the Cr-complex (Cl-Cr-Cl , 171.673°). Due to higher electronegativity value, the two Cl atoms remain apart from each other as much as possible.

Table 3 : Bond lengths, bond angles (within the coordination sphere) of the complexes

Cr-complex, $[\text{Cr}(\text{C}_6\text{H}_{18}\text{N}_4)\text{Cl}_3] \cdot 6\text{H}_2\text{O}$		Fe-complex, $[\text{Fe}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NO}_3)_3] \cdot 6\text{H}_2\text{O}$	
Bond lengths (Å)	Bond angles ($^\circ$)	Bond lengths (Å)	Bond angles ($^\circ$)
Cr(1)-N(2)	2.306	N(2)-Cr(1)-Cl(6)	88.115
Cr(1)-N(3)	2.289	N(3)-Cr(1)-Cl(6)	89.825
Cr(1)-N(4)	2.112	N(4)-Cr(1)-Cl(6)	90.876
Cr(1)-N(5)	2.249	N(5)-Cr(1)-Cl(6)	95.753
Cr(1)-Cl(6)	2.453	N(2)-Cr(1)-Cl(7)	95.364
Cr(1)-Cl(7)	2.515	N(3)-Cr(1)-Cl(7)	83.251
		N(4)-Cr(1)-Cl(7)	84.514
		N(5)-Cr(1)-Cl(7)	90.961
		N(2)-Cr(1)-N(3)	81.239
		N(2)-Cr(1)-N(5)	101.649
		N(4)-Cr(1)-N(3)	89.902
		N(4)-Cr(1)-N(5)	87.264
		Cl(6)-Cr(1)-Cl(7)	171.673
Fe(1)-N(2)	1.875	N(2)-Fe(1)-N(6)	93.690
Fe(1)-N(3)	1.919	N(3)-Fe(1)-N(6)	80.176
Fe(1)-N(4)	1.800	N(4)-Fe(1)-N(6)	94.495
Fe(1)-N(5)	1.918	N(5)-Fe(1)-N(6)	92.709
Fe(1)-N(6)	1.860	N(2)-Fe(1)-N(7)	83.708
Fe(1)-N(7)	1.861	N(3)-Fe(1)-N(7)	86.499
		N(4)-Fe(1)-N(7)	92.705
		N(5)-Fe(1)-N(7)	101.148
		N(2)-Fe(1)-N(3)	86.365
		N(2)-Fe(1)-N(5)	101.150
		N(4)-Fe(1)-N(3)	98.883
		N(4)-Fe(1)-N(5)	74.372
		N(6)-Fe(1)-N(7)	165.683

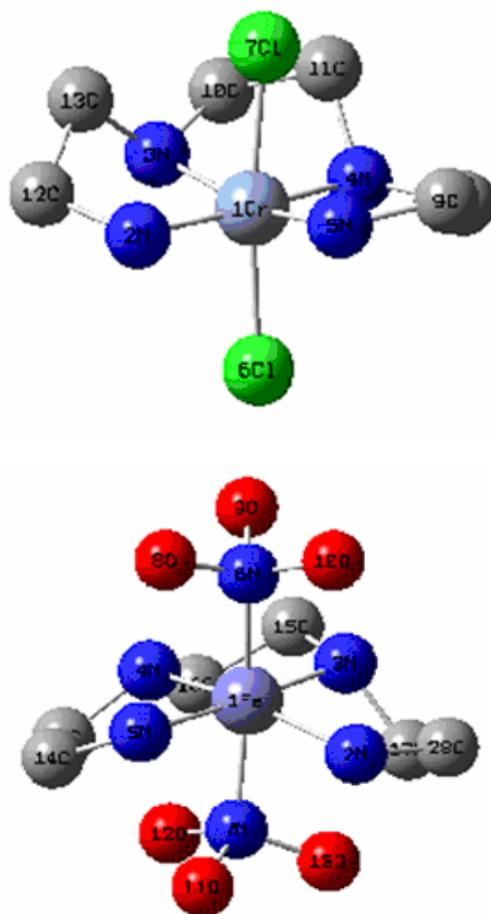


Figure 3 : Model structure of (a) Cr(III)-trien complex and (b) Fe(III)-trien complex. Hydrogen atoms and lone pairs are not shown for clarity.

Table 4 : Energy of the complexes with different geometry

Geometry	Energy (a.m.u)	
	Cr-complex, [Cr(C ₆ H ₁₈ N ₄)Cl ₃]. 6H ₂ O	Fe-complex, [Fe(C ₆ H ₁₈ N ₄)(NO ₃) ₃]. 6H ₂ O
<i>cis-α</i>	-1402.4652	-1098.8631
<i>cis-β</i>	-1404.7691	-1101.6842
<i>trans</i>	-1464.9925	-1141.9911

On the basis of energy (Table 4) we suggested *trans*- geometry for the complexes, since these are energetically more favorable than the *cis*- form. Theoretical energies of the complexes with SCN⁻ and OH⁻ ions as the counter ion were also calculated. In each case the *trans*- geometry complexes were relatively of lower energy. Of the two complexes the energy of iron complex is much higher than that of the chromium complex. This is due to the fact that the charge-charge interaction in iron complex is higher than that in the chromium complex.

Conclusion

Chromium and iron in the +3 state react with triethylenetetramine (trien) in the EtOH medium and produce distorted octahedral complexes with *trans* geometry. Theoretical calculations suggest that two of the counter ions remains attached to the metal ion at the axial position of the octahedron.

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