

Preparation, Characterization and Molecular Models of Some Transition Metal Complexes of Tren [Tren = tris(2-aminoethyl)amine]

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Abstract : Tris(2-aminoethyl)amine, tren, was reacted with Co(II), Ni(II), Cu(II) and Zn(II) in presence of NH₃ and in presence of 4,4'- bipyridyl, separately in the aqueous medium. In all the preparations ClO₄⁻ ion was added as counter ion to get the solid product. The general formulae of the prepared complexes are [M(tren)NH₃](ClO₄)₂ and [M(tren)(C₁₀H₈N₂)](ClO₄)₂. Elemental analysis, IR, UV-visible spectral analysis have been used to characterize the compounds. From powder photographs d-values are reported. Molecular modelling of the compounds have been done to get idea about the structures. Bonding pattern of all the compounds indicate slightly distorted trigonal bipyramidal geometry. Because of steric hindrance of three five membered rings within metal and the ligand, tren, the equatorial plane of the trigonal bipyramid is inclined towards the tripodal ligand.

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Introduction

Five coordinated complexes of first row transition elements are rare. Tris(2-aminoethyl)amine, (tren), has four donor nitrogen atoms and all can participate simultaneously in the bond formation with metal ion. It forms five coordinated trigonal bipyramidal (tbp) complexes where the three equatorial positions and one axial position are occupied by tren itself and the 5th position of the tbp is occupied by a small ligand, molecule or ion. Much studies have been made on metal complexes of different quadridentate tripodal ligands[1-7]. Metal complexes of first row transition metal with quadridentate tripodal ligand tren has rarely been reported [8-10]. A systematic study of tren-metal complex is necessary to get insight about the chemistry of five coordinated metal complexes. In our previous EPR and ENDOR studies[11] we have found that Cu(tren)(SCN)₂ and Cu(tren)NH₃(ClO₄)₂ are trigonal bipyramidal where one SCN ion and NH₃ are at 5th position of the tbp within coordinated sphere of the complexes. The other SCN ion and the ClO₄ ions are present as counter ion.

In the present study we have prepared a number of tris(2-aminoethyl)amine complexes of first row transition elements where NH₃ and 4,4'- bipyridyl are used as secondary ligand in the 5th position of tbp. The EPR and ENDOR study of the complex [Cu(tren)NH₃](ClO₄)₂ has been reported earlier, here it has been included for comparison with other complexes. All the prepared complexes are characterised by chemical analysis and different spectroscopic methods.

Experimental

Materials and methods

Analytical grade (AR) chemicals and ligands were used in the preparation and analytical works (Aldrich, E Merck, and BDH). Micro-analytical data for C, H, N and Cl were obtained from IMRAM, Tohoku University, Japan. Metal contents were determined by complexometric titration[12] and atomic absorption spectrophotometer. FTIR spectra were recorded on a Shimadzu 8300 fourier transform infrared, spectrophotometer and IR spectra were recorded on a Shimadzu IR 470 spectrometer in the range of 4000-400 cm⁻¹ in the form of KBr pellets. Electronic spectra of the complexes were recorded on an UV-160A spectrophotometer between 200-800 nm using nujol mull technique. Melting points were measured in a heating device MEL –TEMP (II), with a FLUKE 51KJ thermometer, USA, in the range 0-400 °C. The specific conductance of the water soluble compounds were measured in the laboratory using a conductometer, CM-55, TOA Electronics Ltd. Tokyo, Japan. Molecular model calculations (MM2) were done using Hyperchem Molecular Modeling Programme (version 5.1), Hyperchem Inc, USA.

Preparation and formulation:

Compounds containing NH₃ as the secondary ligand: Aqueous solutions of tris(2-aminoethyl)amine (1 m mol), corresponding metal salt (1 m mol) and sodium perchlorate (2 m mol), were prepared separately. The three solutions were then refluxed for one hour. After refluxing the solution was gently heated for about an hour to concentrate the solution, NH₃ was added (in excess) and then kept for crystallization at room temperature.

Compounds containing C₁₀H₈N₂ as the secondary ligand: The aqueous solutions of tren (1 m mol), metal salt (1 m mol), 4,4'-bipyridyl (1 m mol) and sodium perchlorate (2 m mol) were mixed and refluxed for about an hour. After refluxing the

solution was gently heated to obtain the desired concentration and then kept for crystallization at room temperature.

After several hours crystalline products were obtained. The crystals were separated by filtration, washed with distilled water and dried over silica gel in a dessicator. The products are stable on exposure to atmosphere. The yield of the prepared compounds were more than 80% on the basis of metal content. The compounds are formulated as :

- i) $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ **A**
- ii) $[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ **B**
- iii) $[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ **C**
- iv) $[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ **D**
- v) $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ **E**
- vi) $[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ **F**
- vii) $[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ **G**
- viii) $[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ **H**

The analytical data and the composition of the compounds are presented in Table 1.

Result and discussion

The composition of the prepared complexes were confirmed by comparing the analytical data for C, H, N, Cl and metal. The calculated and the experimental values are in good agreement. The decomposition temperatures of all the compounds (except the compound **G**) are more than 200 °C. The compound **G**, decomposes in 190-195 °C range. All the compounds are soluble in water and are insoluble in common organic solvents such as MeOH, EtOH, acetone, benzene, CCl_4 .

The IR spectra of the compounds were studied in detail. Both IR and FTIR were recorded, the spectra are basically same but the resolution of the

bands in FTIR are much better. The tentative assignments of the IR bands (Table 2) which are important for understanding of metal ligand bonding, have been done on the basis of the standard references and by comparing with the bands of the ligands and other related compounds [13-15]. The ligand tren absorbs due to asymmetric and symmetric NH stretching vibrations at 3345 cm^{-1} as a doublet and at 2910 cm^{-1} for CH stretching vibration. Besides, the ligand absorbs strongly for $\delta(\text{NH})$, $\nu(\text{CH}_2)$ and $\nu(\text{CN})$ at 1588, 1450 and 1094 cm^{-1} respectively.

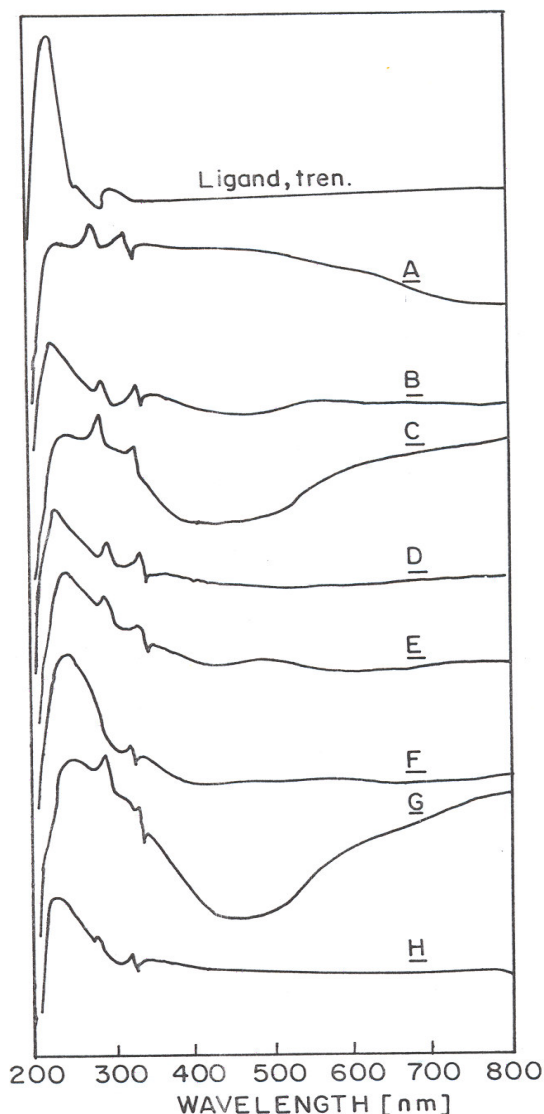
In all the complexes strong and broad peaks in the range $3106\text{-}3338\text{ cm}^{-1}$ and $2901\text{-}3125\text{ cm}^{-1}$ are observed due to NH and CH stretching vibrations respectively. Some times these two peaks overlap each other. The NH bending vibration modes of the compounds are observed as strong bands in the range $1583\text{-}1609\text{ cm}^{-1}$. The CH bending vibration peaks of the CH_2 group of the compounds appeared in the range $1410\text{-}1460\text{ cm}^{-1}$. In case of compounds **E**, **F**, **G**, **H**, the stretching of heteroaromatic unsaturation of 4,4'-bipyridyl appear as pair of bands near 1600 and 1475 cm^{-1} of which the peak at higher wave number overlaps on the NH bending absorption. The CH_2 stretching frequency of these compounds could not be identified may be buried in the other peaks. All the complexes show very strong and broad absorption due to asymmetric stretching and bending mode of vibration of ClO_4^- ion as multiplet in the range $1010\text{-}1140\text{ cm}^{-1}$. The sharp absorption peak of ClO_4^- at 626 cm^{-1} could not be identified. The C-N stretching vibration peaks in the complexes are buried in the broad absorption peaks of the counter ion ClO_4^- . All complexes show absorption peaks for M-N stretching near 500 cm^{-1} region.

Table 1 : Elemental analysis and the decomposition temperature of the complexes

Empirical formula	Decomposition Temp °C	%C Found (Cal)	%H Found (Cal)	%N Found (Cal)	%Cl Found (Cal)	%M Found (Cal)
$[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ A	236-240	16.88 (17.11)	4.95 (5.03)	16.76 (16.63)	16.69 (16.84)	12.05 (14.00)
$[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ B	220-224	18.08 (17.12)	5.21 (5.03)	16.64 (16.64)	16.09 (16.85)	12.84 (13.94)
$[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ C	218-220	16.76 (16.93)	4.69 (4.97)	17.49 (16.45)	16.69 (16.66)	16.45 (14.93)
$[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)](\text{ClO}_4)_2$ D	260-264	16.73 (16.86)	4.21 (4.95)	16.59 (16.38)	16.85 (16.58)	14.64 (15.29)
$[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ E	225-260	35.75 (34.30)	4.33 (4.68)	14.98 (15.00)	12.17 (12.65)	12.47 (10.52)
$[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ F	285-290	34.12 (34.32)	4.60 (4.68)	14.97 (15.01)	12.66 (12.65)	9.76 (10.48)
$[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ G	190-195	34.45 (34.02)	4.93 (4.64)	15.38 (14.88)	12.04 (12.55)	12.72 (11.25)
$[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2$ H	265-269	34.23 (33.91)	4.13 (4.62)	15.08 (14.82)	10.59 (12.51)	12.35 (11.54)

Table 2 : Tentative assignment of important IR bands

Compounds	$\nu(\text{NH})$ cm^{-1}	$\nu(\text{CH})$ cm^{-1}	$\nu(\text{C}=\text{C})/$ $\nu(\text{C}=\text{N})$ Aromatic cm^{-1}	$\delta(\text{NH})$ cm^{-1}	$\nu(\text{ClO}_4^-)$ and $\delta(\text{ClO}_4^-)$ cm^{-1}	$\delta(\text{CH}_2)$ cm^{-1}	$\nu(\text{M}-\text{N})$ cm^{-1}
Tris(2-amino ethyl)amine,	3345	2910		1588		1450	
[Co(tren)(NH ₃)] (ClO ₄) ₂ A	3225	3060		1592	1140-1040	1450	517
[Ni(tren)(NH ₃)] (ClO ₄) ₂ B	3338	2910		1600	1184-1102	1430	481
[Cu(tren)(NH ₃)] (ClO ₄) ₂ C	3245	2915		1586	1133-1078	1410	532
[Zn(tren)(NH ₃)] (ClO ₄) ₂ D	3106	2910		1583	1136-1008	1460	540
[Co(tren)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ E	3225	3080	1592, 1478		1141-1076		566
[Ni(tren)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ F	3165	2960	1595, 1478		1143-1031		503
[Cu(tren)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ G	3230	3125	1585, 1460		1138-1081		534
[Zn(tren)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ H	3195	2990	1591, 1460		1131-1081		535

**Figure 1 :** Uv-visible spectra of the ligand, tren and its complexes

The uv-visible absorption spectra of the ligand and their complexes were investigated. The absorption bands are listed in Table 3 and the spectra are compared in Fig 1 and the bands were assigned on the basis of standard references [16-17]. The ligand Tris(2-aminoethyl)amine, has lone pair of electrons on N. It shows absorption bands at 247 resulting from $n-\sigma^*$ transition. On the other hand 4,4'-bipyridyl has lone pair on N and π -electron in the pyridine ring so it shows intense absorption bands at 298 nm, and 243 nm resulting from $n-\pi^*$ and $n-\sigma^*$ electronic transition respectively. The possible $\pi-\pi^*$ absorption band (near 210 nm) could not be identified. The complexes **A**, **B**, **C**, **D** show almost similar absorptions in the uv-visible spectra. They absorb strongly for $n-\sigma^*$ transitions, like the ligand tren, at the range 240-260 nm. All four complexes absorb strongly due to $n-\pi^*$ transition around 300 nm. There is a band, almost buried in the strong $n-\sigma^*$ band may be due to $\pi-\pi^*$ transition in the counter ion ClO_4^- . In case of compounds **E**, **F**, **G**, **H**, also the uv-visible spectra are similar to each other. They absorb strongly and broadly for $n-\pi^*$ and $n-\sigma^*$ transitions due to tren as well as 4,4'-bipyridyl in same regions like the compounds **A**, **B**, **C**, **D**. The $\pi-\pi^*$ absorption peaks could not be identified. All except Zn complex absorbs strongly and broadly for d-d transitions. But the d-d absorption bands are not well resolved. It is may be due to the fact that the charge transfer (CT) transition near about ~ 360 nm combined with the d-d transition bands giving very big and broad bands. The Zn complexes do not show any d-d transition, since it is a d^{10} system. The similar absorption pattern of the complexes with the ligands demonstrate that no structural change of the ligand occurred due to complexation with metal ions.

Table 3 : Absorption bands of the ligand and the metal complexes:

Compounds	Absorption bands λ_{\max} (nm)			
	d-d	n- π^*	n- σ^*	π - π^*
Tris(2-aminoethyl)amine,			247	
4,4'-bipyridyl		298	243	
[Co(C ₆ H ₁₈ N ₄)(NH ₃)] (ClO ₄) ₂ A	550,430		260	212
[Ni(C ₆ H ₁₈ N ₄)(NH ₃)] (ClO ₄) ₂ B	570		240	213
[Cu(C ₆ H ₁₈ N ₄)(NH ₃)] (ClO ₄) ₂ C	632,535		260	215
[Zn(C ₆ H ₁₈ N ₄)(NH ₃)] (ClO ₄) ₂ D			235	212
[Co(C ₆ H ₁₈ N ₄)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ E	539,470	300	245	
[Ni(C ₆ H ₁₈ N ₄)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ F	553	302	260	
[Cu(C ₆ H ₁₈ N ₄)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ G	750, 620, 530	302	260	
[Zn(C ₆ H ₁₈ N ₄)(C ₁₀ H ₈ N ₂)] (ClO ₄) ₂ H		301	241	

The conductance for dilute solutions of the complexes, were measured taking the formula weight as the molar mass. The observation is that the molar conductance increases rapidly with the dilution of the complex solutions which indicate that these complexes are weak electrolytes.

The pattern of X-ray powder photographs of these compounds are very complicated for indexing and determining the space group. Large number of lines in the powder photographs indicate that these crystals are of lower symmetry. The d-values and their relative intensities are listed in Table 4. Since powder pattern is

the finger print property, the d- values of the complexes recorded here would be extremely useful for further study and reference.

Molecular model calculations of the complex molecules were done using molecular mechanics simulation with MM2 force field [18]. The structures were completely optimised to have the stable structure. All the compounds possess slightly distorted trigonal bipyramidal geometry. The typical models of two types of compounds and the numbering scheme of the atoms in the molecules are shown in Figs- 2a (**A**, **B**, **C**, **D**) and 2b (**E**, **F**, **G**, **H**). Hydrogen atoms and the lone pairs are omitted from the figure for simplicity.

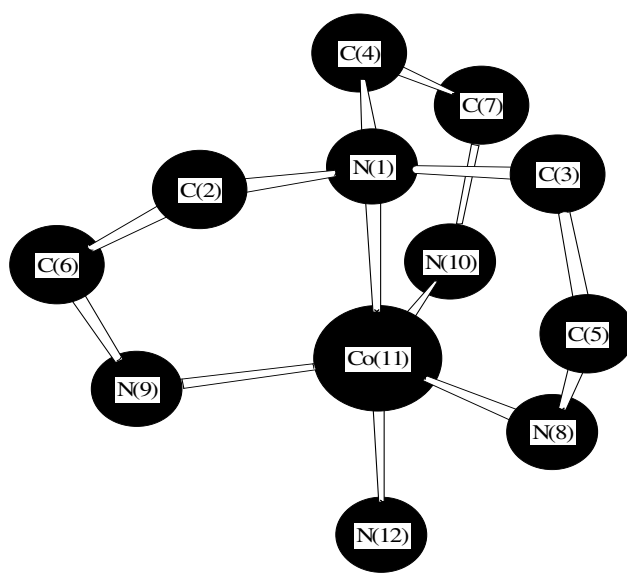


Figure 2a : Molecular model of [Co(C₆H₁₈N₄)(NH₃)](ClO₄)₂. Hydrogen atoms, lone pairs and counter ions are not shown for clarity.

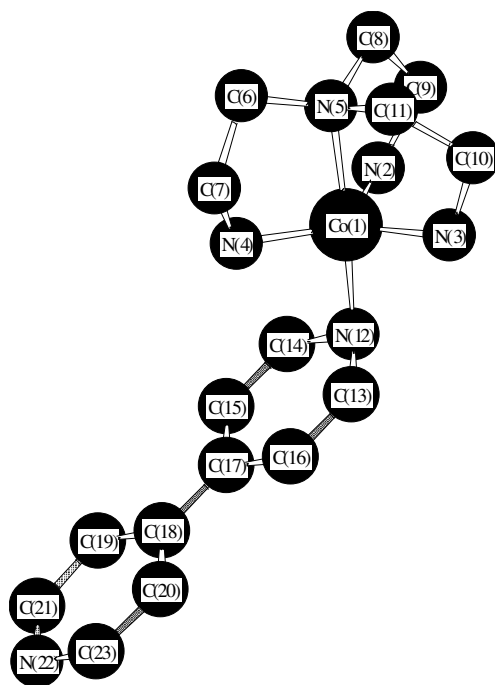


Figure 2b : Molecular model of $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{ClO}_4)_2]$. Hydrogen atoms, lone pairs and counterions are not shown for clarity.

Table 4 : d-values and relative intensities of the lines of x-ray powder photographs of the compounds.

Compounds	d-values and relative intensities
$[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)] (\text{ClO}_4)_2$ A	7.28(m), 5.25(m), 5.16(s), 4.93(s), 4.87(m), 4.80(w), 4.61(m), 4.21(s), 4.16(m), 3.08(w), 3.42(w), 3.31(s), 3.11(w)
$[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)] (\text{ClO}_4)_2$ B	8.36(w), 7.61(m), 7.54(m), 7.46(m), 6.50(w), 5.90(w), 5.78(m), 5.69(m), 5.47(s), 5.06(s), 5.01(s), 4.90(m), 4.67(s), 4.64(s), 4.33(m), 4.25(m), 4.19(m), 4.06(s), 4.04(s), 3.93(s)
$[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)] (\text{ClO}_4)_2$ C	6.67(m), 5.79(w), 4.10(s), 3.49(m), 3.22(w), 3.10(w), 2.81(w), 2.28(w),
$[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{NH}_3)] (\text{ClO}_4)_2$ D	6.70(m), 5.80(m), 4.10(s), 3.67(w), 3.50(s), 3.21(w), 2.8(w), 2.27(w)
$[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)] (\text{ClO}_4)_2$ E	6.34(w), 5.60(w), 5.50(w), 5.25(s), 4.88(s), 4.76(s), 4.55(m), 4.38(m), 4.10(s), 4.04(s), 3.72(m), 3.58(m), 3.52(m), 3.42(m), 3.11(w), 3.03(w).
$[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)] (\text{ClO}_4)_2$ F	6.96(w), 6.29(m), 5.05(w), 5.24(s), 5.20(s), 4.83(m), 4.759(s), 4.68(m), 4.15(w), 4.08(w), 3.76(w), 3.53(w), 3.48(w),
$[\text{Cu}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)] (\text{ClO}_4)_2$ G	7.93(m), 6.93(m), 6.86(m), 6.80(w), 6.20(w), 6.03(w), 5.94(s), 5.87(m), 5.45(w), 5.08(m), 4.63(s), 4.41(w), 4.21(s), 4.17(s), 4.12(s), 4.0(w)
$[\text{Zn}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_{10}\text{H}_8\text{N}_2)] (\text{ClO}_4)_2$ H	8.5(w), 7.20(m), 7.07(w), 6.59(w), 6.49(w), 6.08(w), 5.37(w), 4.82(m), 5.50(w), 4.24(s), 4.14(w).

w = weak, m = medium, s = strong

The metal-ligand bond length and the bond angles specially those in the coordinating sphere are listed in Tables 5a (complexes **A**, **B**, **C**, **D**), & 5b (complexes **E**, **F**, **G**, **H**). The three angles at the equatorial plain are equal and the equatorial bonds are also almost equal in all the complexes. The three angles between equatorial M-N bonds and the axial M-N (N of tren) bond are less than 90° and those between equatorial bonds and the axial M-N(N from ligand at the 5th position) bond are greater than 90°.

This is due to the fact that formation of three five-membered rings by the ligand tren, with metal centre make the equatorial plane inclined towards the ligand tren. Normally Ni form square planer complexes. In this case to make square planer geometry all four coordinating nitrogen atoms of the tripodal ligand, tren, must come to the same plane but because of steric reason it will not be a stable one. So, it forms tpb complex where three of the nitrogen atom (from tripodal ligand) are in the equatorial plan.

Table 5a: Bond length and bond angles in the coordination sphere of the complexes **A**, **B**, **C**, **D**

Bond angles (°)					Bond lengths (Å)				
Compounds	(A)	(B)	(C)	(D)	Compounds	(A)	(B)	(C)	(D)
N(1)-M(11)-N(8)	86.24	87.23	87.10	86.10	N(1)-M(11)	2.003	1.986	1.998	2.045
N(1)-M(11)-N(9)	85.64	87.62	87.48	87.00	N(8)-M(11)	2.082	1.990	2.005	2.079
N(1)-M(11)-N(10)	87.14	88.27	88.00	87.14	N(9)-M(11)	2.084	1.991	2.005	2.081
N(1)-M(11)-N(12)	176.47	178.86	178.95	179.68	N(10)-M(11)	2.084	1.991	2.004	2.081
N(8)-M(11)-N(9)	120.46	120.25	119.93	120.17	N(12)-M(11)	2.040	2.005	2.018	2.076
N(8)-M(11)-N(10)	119.36	121.00	120.17	119.68					
N(8)-M(11)-N(12)	93.91	91.68	91.87	93.54					
N(9)-M(11)-N(10)	119.94	119.28	119.35	119.68					
N(9)-M(11)-N(12)	91.53	92.63	92.84	93.19					
N(10)-M(11)-N(12)	95.9	92.59	92.73	93.03					

Table 5b: Bond length and bond angles in the coordination sphere of the complexes **E**, **F**, **G**, **H**

Bond angles(°)					Bond lengths (Å)				
Compounds	(E)	(F)	(G)	(H)	Compounds	(E)	(F)	(G)	(H)
N(2)-M(1)-N(3)	118.08	125.28	125.45	121.74	N(2)-M(1)	1.896	1.892	1.908	1.979
N(2)-M(1)-N(5)	89.34	93.44	114.64	92.09	N(4)-M(1)	1.900	1.894	1.912	1.976
N(3)-M(1)-N(4)	122.25	119.05	93.37	119.67	N(12)-M(1)	1.864	1.871	1.910	1.947
N(3)-M(1)-N(12)	95.93	91.63	85.00	93.99	N(3)-M(1)	1.902	1.899	1.919	1.977
N(4)-M(1)-N(12)	86.02	81.66	118.76	82.65	N(5)-M(1)	2.012	1.904	1.888	1.997
N(2)-M(1)-N(4)	119.57	114.40	87.87	118.12					
N(2)-M(1)-N(12)	91.22	84.95	92.90	86.41					
N(3)-M(1)-N(5)	83.67	87.92	100.09	86.52					
N(4)-M(1)-N(5)	93.83	100.57	80.82	98.37					
N(5)-M(1)-N(12)	179.45	177.65	178.33	178.48					

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