

PREPARATION AND CHARACTERISATION OF FIRST ROW TRANSITION METAL COMPLEXES WITH QUADRIDENTATE TRIPODAL LIGAND TREN [TREN=TRIS (2-AMINOETHYL) AMINE]

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Isothiocyanato complexes of first row transition metals with quadridentate tripodal ligand, tris(2-aminoethyl) amine, (tren), were prepared and characterized. Empirical formula of the compounds was determined on the basis of elemental analysis. All except Co-compounds have the general formula $[M(\text{tren})\text{NCS}]\text{SCN}$ ($M=\text{Mn(II)}$, Ni(II) , Cu(II) and Zn(II)). In the case of Co-compound, chloride ion remains as counter ion. The bonding pattern of the compounds have been discussed on the basis of IR and UV-visible spectral analysis. The SCN ion, bonded to metal through the N atom, has also been supported by the spectra. X-ray powder pattern of the complexes were also examined.

Key words: Transition metal complexes, Quadridentate tripodal ligand, Tris amine.

Introduction

Five coordinated complexes of first row transition elements are rare. It has been shown that tripod like quadridentate ligands are particularly capable of forming five coordinated complexes with transition metals. The tripodal ligands are bulky and polydentate, as a result the crowding around the metal ion prevents the formation of six coordinated complexes. The structure of a typical five coordinated complex with tripodal ligand is shown in Fig 1. Preparation characterization and different physical and chemical properties of five coordinated trigonal bipyramidal (tbp) complexes of first row transition metals with tripodal ligands, tris (2-dimethyl aminoethyl) amine (trenMe) (Ciampolini and Nardi 1966 a & b), tris (2-methylthioethyl) amine (TSN) (Ciampolini *et al* 1968), TPyEA (Di Vair and Mani 1983) etc have been reported. In most of the cases five coordinated tbp complexes and in few cases four coordinated tetrahedral complexes were obtained. Nickel forms five coordinated complexes with relatively more crowded ligand and six coordinated complexes with less crowded ligand (Hall and Woulf 1958; Ciampolini *et al* 1968). The crystal structures of tbp copper complex of tris (2-aminoethyl) amine (tren) containing NH_3/SCN at the 5th position of tbp have also been reported (Dugan *et al* 1980; Jain and Lingafelter 1967). Earlier, we had reported (Ehsan *et al* 1996) the ESR and ENDOR spectral analysis of $\text{Cu}(\text{tren})(\text{SCN})_2$ and $\text{Cu}(\text{tren})\text{NH}_3(\text{ClO}_4)_2$ doped in $\text{Zn}(\text{tren})(\text{SCN})_2$ and $\text{Zn}(\text{tren})\text{NH}_3(\text{ClO}_4)_2$, respectively, where it was shown that the geometry of one Cu-complex is trigonal bipyramidal with one SCN ion at the 5th position of tbp (within the coordination sphere of copper) bonded to copper

atom through N-atom of SCN and the other SCN ion remains as counter ion, and the order complex $[\text{Cu}(\text{tren})\text{NH}_3(\text{ClO}_4)_2]$ is also tbp with NH_3 at the 5th position of tbp and ClO_4^- ions remain as counter ion.

The ligand, tren, quadridentate amine has four donor nitrogen atoms and all simultaneously participate in the bond formation with metal ion. Here we are reporting the preparation and characterization of a series of isothiocyanato complexes of tren with Mn(II) , Co(II) , Ni(II) , Cu(II) and Zn(II) having similar empirical formulae.

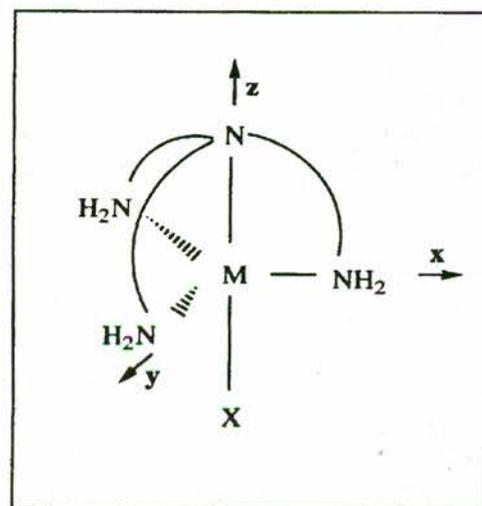


Fig 1. Structure of typical trigonal bipyramidal (tbp) complex formed by tripodal ligand. Three equatorial positions and one axial position of tbp are coordinated by the tripodal ligand and at the 5th position small molecules or ions, X may be coordinated.

Materials and Methods

The ligand tren was procured from Wako Pure Chemical Company, Japan and was used without further purification. Other chemicals and solvents, metal salts used in all preparative and analytical works were of analytical grade (BDH and Aldrich). Micro-analytical data for C, H and N were obtained from the Institute for Chemical Reaction Science, Tohoku University, Japan. IR spectra of the compounds were recorded on a Shimadzu IR spectrophotometer, Model IR 470 of Japan in the region of 4000-400 cm^{-1} using KBr pellet and the IR spectrum of the ligand (liquid) was recorded as thin film between NaCl cells. The electronic spectra of the complexes were recorded with nujol in a Shimadzu UV-visible recording spectrophotometer, Model UV-160A, in the wave length range 200-1100 nm. The X-ray powder diffraction photographs were obtained using a Debye Scherrer camera (diameter 57.3 mm) and nickel filtered Co- K_{α} radiation (1.79 Å°).

Preparation of the complexes. All the compounds were prepared following a general procedure. The ligand (1 mmol) was first reacted with 1 mmol of corresponding metal chloride, $\text{MCl}_2 \cdot x\text{H}_2\text{O}$, at room temperature, in ethanol, using a magnetic stirrer. The solid complex compound was preprecipitated out when ethanol solution of NH_4SCN (2 mmol) was added to the reaction mixture as counter ion. The coloured solid products

were separated by filtration, washed with EtOH and dried over silica gel. The empirical formula of the compounds were determined by comparing the elemental analysis data and are tabulated in Table 1.

Results and Discussion

The complexes were prepared by straight forward reaction between ligand and the metal salt in nonaqueous solvent (EtOH). The product was obtained within short time of addition of the counter ion. The experimental and calculated values of C, H, and N of the complexes are in good agreement. The assignment of important IR bands of the ligand and the complexes have been done on the basis of standard references and are described in Table 2 (Cross 1964; Bellamy 1975; Nakamoto 1978).

The IR absorption bands of the ligand are very much broad whereas the IR spectra of the metal complexes are very sharp and highly resolved. The NH stretching frequency of the complexes are at slightly lower field than that of the free ligand, which indicated the bond formation between metal and N-atoms of the ligand. In the case of all complexes, there is a sharp strong absorption for $\text{C}\equiv\text{N}$ of the SCN group at the 5th position of tbp. This absorption is relatively at lower frequency ($<2100 \text{ cm}^{-1}$) which is an indication that the SCN

Table 1
Colour and elemental analysis of the complexes

Complexes	Colour	%C	%H	%N	%S
		found(calc)	found(calc)	found(calc)	found(calc)
[Mn(tren)NCS]SCN	A dark brown	29.47 (30.28)	6.19 (5.68)	25.90 (26.50)	19.76 (20.19)
[Co(tren)NCS]Cl	B red	27.96 (28.15)	5.87 (6.03)	23.76 (23.46)	9.82 (10.72)
[Ni(tren)NCS]SCN	C violet	30.16 (29.93)	5.60 (5.61)	25.72 (26.19)	
[Cu(tren)NCS]SCN	D blue	29.75 (29.49)	5.38 (5.52)	25.35 (25.80)	
[Zn(tren)NCS]SCN	E white	29.66 (29.31)	5.62 (5.49)	25.02 (25.64)	

Table 2
IR bands of the complexes

Complexes	NH	CH	NH	CH	$\text{C}\equiv\text{N}$	CS	(NCS)
	stretch cm^{-1}	stretch cm^{-1}	bending cm^{-1}	bending cm^{-1}	stretch cm^{-1}	stretch cm^{-1}	bending cm^{-1}
Ligand	3350	2930	1588	1449			
[Mn(tren)NCS]SCN	A 3310	2935	1589	1453	2060	856	490
[Co(tren)NCS]Cl	B 3480	2998	1579	1448	2090	822	456
[Ni(tren)NCS]SCN	C 3300	2990	1578	1457	2085	850	463
[Cu(tren)NCS]SCN	D 3275	2970	1591	1458	2080	814	467
[Zn(tren)NCS]SCN	E 3275	2945	1591	1459	2080	880	470

group is attached to the metal ion through N-atom producing isothiocyanato complexes. The relatively higher position of CS stretching bands of the complexes further proves that the SCN group is attached to the metal through N-atom and the S-atom remains free. Besides these, all the complexes and the ligand show absorption band for stretching and bending mode of vibration of CH at more or less at the same position as these are not affected by the presence of metal in the system.

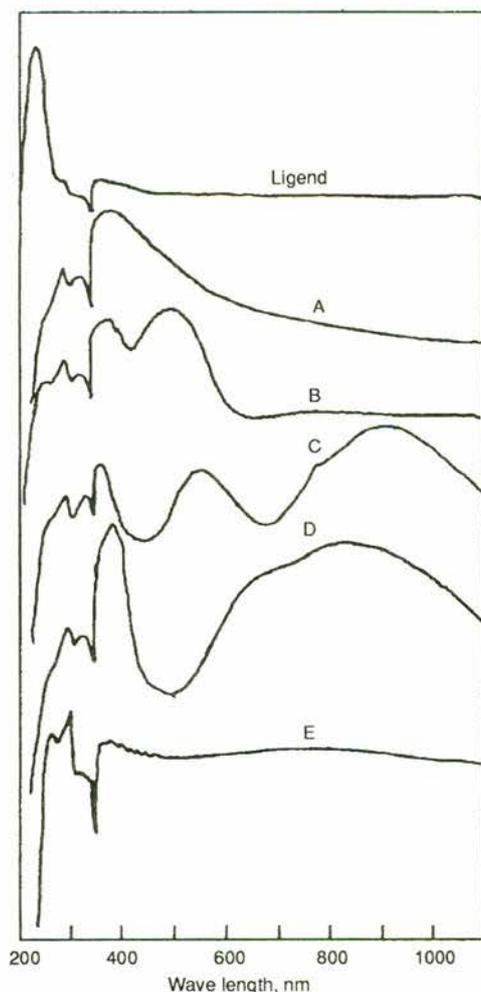


Fig 2. Electronic spectra of tren and its metal complexes.

Table 3
Assignments of electronic spectra of the complexes

Compounds	$\pi \rightarrow \theta^*$ (nm)	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)	CT (nm)	d-d (nm)
Ligand	247	300	343		
[Mn(tren)NCS]SCN A	256	299	341	376	800
[Co(tren)NCS]Cl B	260	298	340	374	505
[Ni(tren)NCS]SCN C	259	298	338	363	562,795,925
[Cu(tren)NCS]SCN D	258	299	339	385	660,830
[Zn(tren)NCS]SCN E	261	299	335	358	

The electronic spectra of the complexes are compared with that of the ligand in Fig 2. The signals of electronic spectra of the ligand and the complexes were analyzed on the basis of standard references and are tabulated in Table 3 (Lever 1968; Robert and Caserio 1977).

The ligand tren shows very strong absorption at 247 nm for $n \rightarrow \sigma^*$ transition of lone pair of amino nitrogens (4N) to the antibonding σ orbital of the C-N bond. The ligand shows two more weak absorptions at 300 and 343 nm which could not be identified. In the case of metal complexes, the nitrogen lone pairs are coordinated to metal atoms; as a result the $n \rightarrow \sigma^*$ absorption bands (A 256, B 260, C 259, D 258, E 261 nm) are shifted towards high wavelength region and the intensity becomes weaker. In the UV region within 200-350 nm range all the complexes show strong absorption due to $\pi \rightarrow \pi^*$ transition (A 299, B 298, C 298, D 299, E 299 nm) and $n \rightarrow \pi^*$

Table 4
d-values of the compounds

Compound	d-values (A°) and relative intensity
[Mn(tren)SCN]SCN A	1.15(w), 1.07(w), 1.06(s), 1.04(w), 1.02(w), 1.00(m), 0.98(vw), 0.97(vw), 0.95(w), 0.94(w), 0.93(w), 0.93(w) and 0.92(vw).
[Ni(tren)SCN]SCN C	1.59(w), 1.50(w), 1.46(w), 1.37(w), 1.31(w), 1.25(w), 1.20(s), 1.18(w), 1.15(m), 1.13(m), 1.11(w), 1.10(m), 1.07(s), 1.04(s), 1.03(s), 1.02(s), 0.99(s), 0.98(s), 0.97(s), 0.97(m), 0.96(w), 0.95(m), 0.94(w), 0.94(vs), 0.93(m), 0.93(w), 0.92(w), 0.92(w) 0.92(m) and 0.92(m).
[Cu(tren)SCN]SCN D	1.09(vw), 1.02(w), 1.00(w), 0.99(w), 0.98(w), 0.97(w), 0.95(w), 0.94(w), 0.93(w), 0.92(w) and 0.91(w).
[Zn(tren)SCN]SCN E	1.36(w), 1.32(w), 1.25(w), 1.22(w), 1.19(m), 1.18(w), 1.15(w), 1.12(w), 1.09(w), 1.08(w), 1.05(m), 1.04(m), 1.02(m), 1.01(m), 1.00(m), 0.99(m), 0.99(w), 0.98(w), 0.97(m), 0.97(m), 0.96(s), 0.95(m), 0.94(s), 0.94(w), 0.93(m), 0.93(s), 0.92(m) and 0.92(m).

transitions (A 341, B 340, C 338, D 339, E 335 nm) of the multiple bonds present in the counter ions. Above 350 nm, all the compounds show the charge transfer (CT) transition (A 376, B 374, C 363, D 385, E 385 nm) between the central metal atom and the ligand moiety. In the visible region, all the complexes, except A and E, show absorption for d-d transitions (B 505, C 562, 795, 925, D 660, 830 nm) in the metal atoms. The compound E does not show any absorption for d-d transition since it is a d^{10} system. In case of Mn-compound, very weak d-d transition absorptions are masked by the tail of ligand absorption and the CT transition (at 376 nm) between Mn and ligand.

Attempts to grow single crystals to determine complete crystal structures were not successful. The X-ray powder photographs of the compounds were taken. The d-values (in \AA unit) and their relative intensities are listed in Table 4. The powder pattern are very much complicated for indexing and space group determination. Large number of lines in the powder photographs indicate that the crystals are of lower symmetry. But since the powder pattern is fingerprint property of complexes, the d-values recorded here would be extremely useful for further study and references.

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