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PREPARATION, CHARACTERIZATION AND MOLECULAR MODELS OF THE COMPLEXES OF QUADRIDENTATE TRIPODAL LIGAND TREN [TREN = TRIS(2-AMINOETHYL)AMINE] WITH Ag(I), Cd(II), Hg(II), Zr(IV) AND U(VI)

M Q Ehsan [a]****, M H Rashid*** [a] ***and S M Saiful Islam*** [b]

[a]*Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh*

[b]*Department of Chemistry, Shahjala University of Science and Technology, Sylhet, Bangladesh*

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The tripodal ligand tren, has been reacted with Ag(I), Cd(II), Hg(II), Zr(IV) and U(VI) in the EtOH medium. The solid product obtained immediately after the reaction, were formulated by comparing C, H, N, and S analysis data. Ag(I) and Cd(II) form simple five coordinated compounds and the others produce double salt like compounds. The bonding patterns of the compounds have been discussed on the basis of IR an UV visible spectral analysis. The geometry of the coordination sphere of the complexes are suggested on the basis of molecular models.

Key words: Tripodal ligand, Coordination sphere, Molecular model.

Introduction

The tripod like ligands produce five coordinated complexes rather than six coordinated one, with transition metals, due to their quadridentate property and to avoid steric hindrance (Ciampolini and Nardi 1966 a & b; Ciampolini *et al* 1968; Di Vaira and Mani 1983). In our previous communications (Ehsan 2000; Ehsan and Islam 2000), it was shown that the ligand tren reacts with first row transition metals in 2^+ and 3^+ oxidation state, to give five coordinated complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). The divalent metal ions produce five simple coordinated complexes whereas, the trivalent metal ions produce double salt like compounds. In this communication, we report the preparation and characterization of the tren complexes with heavy metals Ag(I), Cd(II), Hg(II), Zr(IV) and U(VI). The molecular geometry of the complexes are reported here on the basis of molecular models.

Experimental

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 pellets 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 200-1100nm. The molecular model of the compound was made using a Hyperchem Molecular Modeling programme (version 5.1), Hyperchem Inc, USA.

Preparation. All the compounds were prepared by direct reaction between metal salt and the ligand in the EtOH medium. The ligand (1 mmol) and the corresponding metal salt (1 mmol) solutions in EtOH were prepared separately and then mixed together on a magnetic stirrer at room temperature. Solid powdered product separated out immediately after mixing. In case of Hg and UO_2- complexes, NH_4SCN was mixed with metal salt before adding to the ligand solution. The solid products were separated by filtration, washed with EtOH and dried over silica gel. The compounds were stable in light and air. The empirical formulas of the compounds which were determined by comparing the elemental analysis data in Table 1 are

A $[Ag(tren)NO_3]$
B [Cd(tren)NCS]SCN
C $[Hg(tren)Cl]Cl.HgCl_2$
D $[ZrO(tren)Cl]Cl.ZrOCl_2$ and
E $[UO_2(tren)NCS]SCN.UO_2(CH_3COO)_2$

Results and Discussion

The complexes were prepared by straight forward reaction between ligand and the metal salt in nonaqueous solvent

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*Author for correspondence

Table 1
Elemental analysis of the complexes

Compounds	Colour	Decomp Temp. ℃	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)	% S Found (Calc.)
A $[Ag(tren)NO_3]$	White	380 - 384	22.60 (22.79)	5.37 (5.73)	21.77 (22.15)	
B $[Cd(tren)NCS]SCN$	White	294 - 300	25.58 (25.63)	4.93 (4.84)	22.41 (22.42)	17.20 (17.08)
C $[Hg(tren)Cl]Cl.HgCl_2$	White	365 - 370	10.72 (10.46)	2.62 (2.63)	7.97 (8.12)	
D $[ZrO(tren)Cl]Cl.ZrOCl_2$	Greenish white	374 - 378	14.07 (13.84)	4.14 (3.87)	10.30 (10.76)	
E $[UO_2(tren)NCS]SCN.UO_2(CH_3COO)_2$	Yellowish	455 - 460	15.21 (15.72)	3.01 (2.64)	9.81 (9.14)	7.63 (7.01)

Table 2
Assignment of important IR bands.

Complexes	NH Stretch cm^{-1}	CH Stretch cm^{-1}	NH Bend cm^{-1}	NO_3^- cm^{-1}	SCN cm^{-1}	MN Stretch cm^{-1}
A $[Ag(tren)NO_3]$	3295	2910	1600	ν(1434) ν(888)		578
B $[Cd(tren)NCS]SCN$	3120	2935	1579		ν(2065) CN ν(855) CS	592
C $[Hg(tren)Cl]Cl.HgCl_2$	3295	2930	1583			529
D $[ZrO(tren)Cl]Cl.ZrOCl_2$	3400 - 2910		1570			
E $[UO_2(tren)NCS]SCN.UO_2(CH_3COO)_2$	3215	2910	1587		ν(2070) CN ν(880) CS	515

(EtOH). In all cases the product was obtained immediately after mixing the ligand and the metal salt. The experimental and calculated values of C, H, N, and S of complexes are in good agreement which demonstrate that the compounds are pure enough and support the proposed formulations. The assignment of important IR bands of the ligand and complexes have been done on the basis of standard references and are listed in Table 2 (Cross 1964; Bellamy 1975; Nakamoto 1978; Ehsan 2000).

The IR spectra of all the metal complexes except **D** are very sharp and well resolved. The spectrum of the ligands is broad and that of the **D**, is very much broad. All the complexes absorb for NH stretching of primary amino groups of the ligands moiety, as doublet about 3120-3400 cm^{-1} frequency, which is at slightly lower field than that of the free ligand, indicating the bond formation between metal and N-atoms of the ligand. The complexes absorb for CH stretching (of CH_2 group) at 2910-2935 cm^{-1} range. The position of stretching vibration of CH are more or less at same position to that of the ligand, since these are not affected by the presence of metal in the system. In case of compound **D**, both NH and CH stretching bands appear as a broad band at 2910-3400 cm^{-1} region. The complexes **B** and **E** show strong absorption for C≡N stretching of the SCN group at about 2000 cm^{-1}, which is relatively at lower position than that of the normal position. This is an indication that SCN group is attached to the metal ion through the N-atom and S atom remains free, producing isothiocyanato complexes. The relatively high position of CS stretching bands further supports that the S atom of SCN group remains free. In case compound **A**, there is NO_3^- ion at the fifth position of the trigonal bipyramid (tbp). The presence of the NO_3^- ion in the compound is well indicated in it's IR spectrum. It shows very strong NO_3^- stretching band at 1434 cm^{-1} and bending

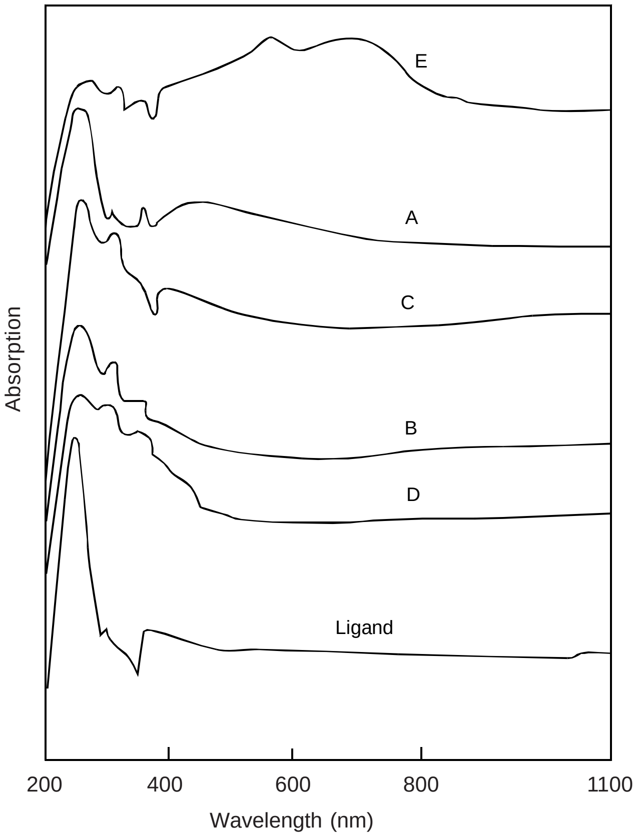

Fig 1. Electronic spectra of the ligand, tren and its metal complexes.

absorption at 888 cm^{-1}. The absorption bands of the complexes in the range 515-592 cm^{-1} are suggested for M-N stretching.

The electronic spectra of the complexes are compared with that of ligand in Fig 1. The signals of eletronic spectra of the ligand and the complexes were analyzed on the basis of standard references and are tabulated in Table 3 (Lever 1968; Roberts and Casserio 1977; Ehsan 2000, Ehsan and Islam 2000). The ligand tren shows very strong absorption at 247 nm for

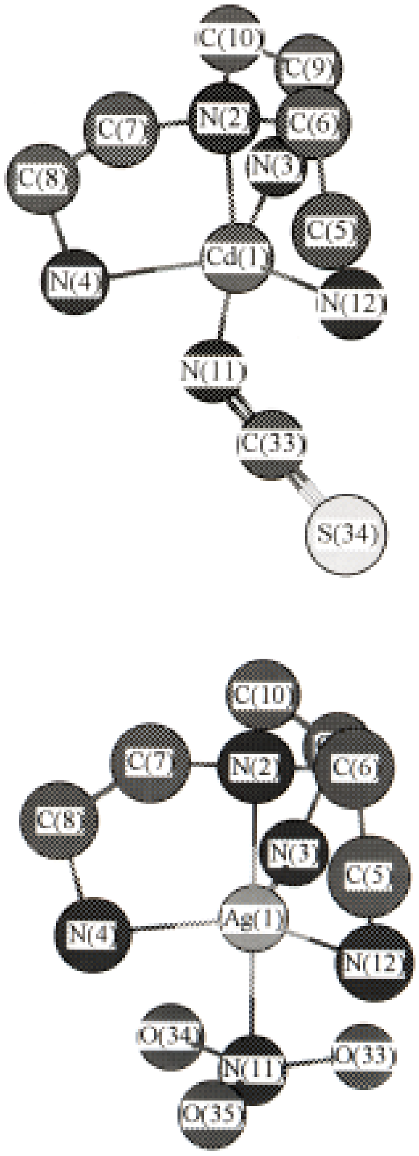

Fig 2(a). Slightly distorted trigonal bipyramidal coordination environment around Cd-atom (b) Spherically symmetric tbp coordination environment around Ag-atom.

Table 3
Assignments of electronic spectra of the complexes

Compounds		Electronic absorption bands (nm)				
Ligand		247	300	343		
$[Ag(tren)NO_3]$	**A**	245	300	342		
$[Cd(tren)NCS]SCN$	**B**	245	299	323	368	
$[Hg(tren)Cl]Cl.HgCl_2$	**C**	245	298		361	
$[ZrO(tren)Cl]Cl.ZrOCl_2$	**D**	252	299	340		420
$[UO_2(tren)NCS]SCN.UO_2(CH_3COO)_2$	**E**	252	299	341		514, 625

Fig 2. Molecular models of the tren -metal complexes showing almost spherically symmetrical trigonal bipyramidal coordination environment in the Ag and Hg-compounds, slightly distorted trigonal bipyramidal structure of Cd-compound and slightly distorted octahedral structure of U-compound.

n-σ* transition of lone pair of amino nitrogens (4N) to the antibonding σ orbital of the C-N bond. The ligand shows two more very weak absorptions at 300 and 343 nm which could not be identified (Table 3).

The spectra of all the complexes in the 200-350nm range are almost similar to that of the ligand, which demonstrate that after complexation no structural change of the ligand has occurred. Strong absorption in the range 245-252 nm are due to n→σ* transition of the nitrogen lone pair of the ligand. Like the lignad, the complexes show unidentified and very weak absorptions at 300 and 343 nm range. In case of first row transition metals complexes of tren (Ehsan 2000), these two absorption peaks (near 300 and 343 nm) were more intense than that of the n→σ* transition. Complexes **B** and **C** show

Table 4a

Bond lengths and bond angles in the coordination sphere of the complexes of Ag(I), Cd(II), and Hg(II)

Parameters	Ag - complex		Cd - complex		Hg - complex	
Bond length(Å)	Ag(1)-N(2)	2.066	Cd(1)-N(2)	2.182	Hg(1)-N(2)	2.150
	Ag(1)-N(3)	2.095	Cd(1)-N(3)	2.215	Hg(1)-N(3)	2.191
	Ag(1)-N(4)	2.095	Cd(1)-N(4)	2.215	Hg(1)-N(4)	2.191
	Ag(1)-N(11)	2.034	Cd(1)-N(11)	2.157	Hg(1)-Cl(11)	2.465
	Ag(1)-N(12)	2.097	Cd(1)-N(12)	2.210	Hg(1)-N(12)	2.191
Bond angle (◦)	N(2)-Ag(1)-N(3)	89.152	N(2)-Cd(1)-N(3)	87.131	N(2)-Ag(1)-N(3)	92.726
	N(2)-Ag(1)-N(4)	89.266	N(2)-Cd(1)-N(4)	87.295	N(2)-Ag(1)-N(4)	92.759
	N(2)-Ag(1)-N(11)	180.000	N(2)-Cd(1)-N(11)	161.076	N(2)-Ag(1)-Cl(11)	180.000
	N(2)-Ag(1)-N(12)	89.275	N(2)-Cd(1)-N(12)	87.544	N(2)-Ag(1)-N(12)	92.838
	N(3)-Ag(1)-N(4)	119.424	N(3)-Cd(1)-N(4)	117.062	N(3)-Ag(1)-N(4)	119.297
	N(3)-Ag(1)-N(11)	90.827	N(3)-Cd(1)-N(11)	82.803	N(3)-Ag(1)-Cl(11)	87.344
	N(3)-Ag(1)-N(12)	120.717	N(3)-Cd(1)-N(12)	121.301	N(3)-Ag(1)-N(12)	120.155
	N(4)-Ag(1)-N(11)	90.792	N(4)-Cd(1)-N(11)	83.120	N(4)-Ag(1)-Cl(11)	87.295
	N(4)-Ag(1)-N(12)	119.802	N(4)-Cd(1)-N(12)	120.989	N(4)-Ag(1)-N(12)	119.851
	N(11)-Ag(1)-N(12)	90.687	N(11)-Cd(1)-N(12)	111.378	Cl(11)-Ag(1)-N(12)	87.036

Table 4b

Bond lengths and bond angles in the coordination sphere of the complexes of Zr(IV) and U(VI)

Parameters	ZrO - compound		UO$_2$ - compound	
Bond length (Å)	Zr(1)-N(2)	2.156	U(1)-N(2)	1.856
	Zr(1)-N(3)	2.189	U(1)-N(3)	1.910
	Zr(1)-N(4)	2.189	U(1)-N(4)	1.934
	Zr(1)-N(11)	2.090	U(1)-N(11)	1.750
	Zr(1)-N(12)	2.183	U(1)-N(12)	1.901
			U(1)-N(15)	1.770
Bond angle (◦)	N(2)-Zr(1)-N(3)	87.885	N(2)-U(1)-N(3)	94.483
	N(2)-Zr(1)-N(4)	88.019	N(2)-U(1)-N(4)	92.670
	N(2)-Zr(1)-O(11)	167.320	N(2)-U(1)-O(11)	175.014
	N(2)-Zr(1)-N(12)	88.229	N(2)-U(1)-N(12)	94.784
	N(3)-Zr(1)-N(4)	117.921	N(2)-U(1)-O(15)	96.646
	N(3)-Zr(1)-O(11)	85.538	N(3)-U(1)-N(4)	103.207
	N(3)-Zr(1)-N(12)	120.867	N(3)-U(1)-O(11)	80.990
	N(4)-Zr(1)-O(11)	85.885	N(3)-U(1)-N(12)	105.099
	N(4)-Zr(1)-N(12)	120.867	N(3)-U(1)-O(15)	168.796
	O(11)-Zr(1)-N(12)	104.450	N(4)-U(1)-O(11)	86.367
			N(4)-U(1)-N(12)	150.017
			N(4)-U(1)-O(15)	75.005
			O(11)-U(1)-N(12)	88.453
			O(11)-U(1)-O(15)	87.839
			N(12)-U(1)-O(15)	75.302

CT transition at 368 and 361 nm respectively, but there is no d→d transition since they are d^{10} system. Complexes **A**, **D** and **E** show d→d transitions at 430, 420, and 514, 625 nm, respectively. These complexes may show CT transitions which are buried in the d→d transition bands.

Molecule modeling of the compounds were done by molecular mechanics with MM^+ force field, (Hyperchem 1996) using commercially available computer programme of Hyperchem Inc, USA The structure was completely minimized to get the most stable state. The model of Ag and Cd-compounds and the numbering scheme are shown in Fig 2, and the bond angles and bond lengths are shown in Table 4a.

On the basis of models, the geometry of the coordination sphere of the complexes are suggested as trigonal bipyramidal (tbd). In case of compounds **A** and **C** the ligand at the 5th position of tbp are symmetrical (NH_3 in **A** and Cl in **C**), as a result the coordination geometry around the metal atom is almost spherically symmetric trigonal bipyramidal (tbp). In both cases equatorial bond lengths and bond angles are same. Axial bonds are in same straight line but the axial bond lengths are different. In both the compounds, the metal-5th ligand bond is longer than the other. In case of compound **B**, the unsymmetrical group (SCN) at the 5th position of tbp, make a slightly distorted (tbp) coordination environment around the metal atom shown in Fig 2a and 2b. Each bonds and bond angles in the coordination sphere (axial and equatorial) are slightly different from each other. The values of bond angles and bond lengths and their trends, of all the compounds are fairly comparable to crystallographic data for the compounds $[Cu(tren)NH_3]\,(CIO_4)_2$ and [Cu(tren)NCS] SCN (Jain and Lingafelter 1967; Dugan *etal* 1980).

The coordination phenomena of the ZrO^- and UO^{-2} compounds are little different. No secondary ligand except 'tren' is coordinated to the metal atom. As a result we get slightly distorted tbp geometry around Zr-atom with one O-atoms linked to U-atom. The bond lengths and bond angles in the coordination sphere of these two compounds are listed in Table 4b.

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