

MAGNESIUM(II) COMPLEXES OF TRIAZENE-1-OXIDES

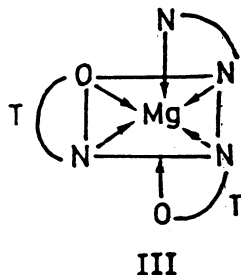
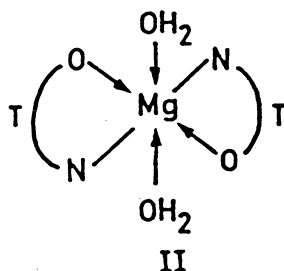
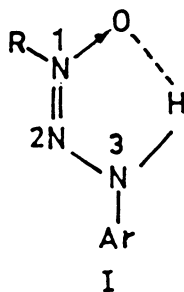
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Magnesium(II) derivatives of triazene-1-oxides (TH) have been reported. The preparation of the derivatives has been achieved by interacting alcoholic solution of (TH) with (i) magnesium chloride-hydroxide and (ii) magnesium metal magnesium oxide. Mixed-ligand complexes of magnesium(II) were prepared by reacting $MgT_2 \cdot 2H_2O$ chelates with *o*-phenanthroline/dipyridyl in 1 : 1 molar ratio in acetone. Structural investigations have been done by elemental analyses, conductance, molecular weight and I.R. spectral studies.

INTRODUCTION

Magnesium(II) complexes, though much less studied, are found to exhibit a variety in its coordination potentialities from four-coordinate¹ $[NMe_4]_2MgCl_4$ through five-coordinate² $[Mg(OAsMe_3)_5](ClO_4)_2$ and six-coordinate $[Mg(NH_3)_6]Cl_2$. Chlorophylls are an important exception to the above coordination preferences of magnesium(II) consisting of tetrapyrrole systems. The environment for magnesium(II) has been found to be rigid and planar. In the present communication an attempt has been made to study the coordination behaviour of magnesium(II) using substituted monobasic bidentate triazene-1-oxides (TH), (I) and their mixed complexes using *o*-phenanthroline and dipyridyl. Magnesium(II) complexes of triazene-1-oxides are of the type (II) and their mixed chelates of the type (III). The substituents of the triazene-1-oxides are represented by *o*-, *m*-, and *p*- and are counted from the N-C(Ar) bond.



EXPERIMENTAL

Ligands were synthesized following published procedures,³ *i.e.* by coupling substituted hydroxyl amines with benzene diazonium chloride at 0-5°C using

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sodium acetate to control pH. The crude product was recrystallised from ethanol or aqueous ethanol. Magnesium(II) complexes of triazene-1-oxides were obtained by two different methods:

(a) To 2.0 g of hot magnesium chloride solution, ammonium hydroxide solution (in presence of ammonium chloride) was added gradually with stirring till alkaline. The precipitate of magnesium hydroxide obtained was washed with water and then refluxed with aqueous-alcoholic or alcoholic solution of triazene-1-oxides in 1 : 2 and 1 : 3 molar ratios till the hydroxide dissolved. The solution was filtered, concentrated and cooled when crystals of magnesium(II) chelates came out. The crystals were filtered under suction and dried in a desiccator.

Magnesium(II) chelates obtained from above were taken in acetone and reacted with *o*-phen/dipy in 1 : 1 molar ratio under reflux. The clear solution was filtered and concentrated when crystals separated out. The crystals were filtered washed with alcohol and dried.

(b) 0.25 g of clear magnesium ribbon was converted into oxide by heating in a vetroasil crucible, transferred to a reflux flask and suspended in alcohol. To this suspension aqueous-alcoholic or alcoholic solutions of triazene-1-oxide were added in 1 : 2 and 1 : 3 molar ratios and the mixture refluxed till a clear solution was obtained. The solution was filtered, concentrated and cooled when crystals of magnesium(II) chelates separated out. The crystals were filtered, washed with alcohol and dried in a desiccator.

Magnesium(II) chelates obtained from above were taken in acetone and reacted with *o*-phen/dipy in 1 : 1 molar ratio under reflux. The clear solution was filtered under suction and concentrated when crystals came out. The crystals were filtered, washed with acetone and dried.

Magnesium(II) chelates obtained by both methods were recrystallised from minimum volume of acetone and reprecipitated by the addition of petroleum-ether with stirring.

The yield and the size of the crystals of magnesium(II) chelates obtained from the first method was better than the second method. It appears that the protons liberated from the triazene-1-oxide ligands are taken up by the hydroxide ions relatively more quickly and the pH of the reaction medium is not allowed to change.

Magnesium was determined as pyrophosphate after decomposing the complexes with 1 : 1 HCl. Conductivity measurements were made in nitromethane using Philip's conductance bridge and molecular weights were determined in freezing benzene. C, H determinations and I.R. spectra in the range of 4000–200 cm^{-1} in CsI discs were recorded at C.D.R.I., Lucknow.

RESULTS AND DISCUSSION

Magnesium(II) chelates of triazene-1-oxides are of the type $\text{MT}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MT}_2 \cdot o\text{-phen/dipy}$ (Table 1). The chelates are neutral and monomer. The i.r. spectra indicate the bonding of H_2O to magnesium(II). The bondings of N-atom

and N-O-atom of triazene-1-oxide ligands are also indicated by the disappearance of N-H stretch and lowering of the $\overset{1}{N} \rightarrow \overset{1}{O}$ vibrational frequency.

Magnesium, the second-row element, has a chemistry intermediate between that of Be and the heavier elements. It has considerable tendency to covalent bond formation, consistent with the high charge/radius ratio. Magnesium(II) belongs to class (A) acceptor and, therefore, with a few exceptions, forms complexes that exist in the solid state and dissociate in aqueous solution. An important exception to this rule is provided by the magnesium complexes of tetrapyrrole systems. The most important of such derivatives are the chlorophylls and related compounds.

TABLE 1
CHARACTERIZATION DATA OF MAGNESIUM (II) CHELATES OF TRIAZENE-1-OXIDES (TH) AND MIXED CHELATES WITH *o*-PHEN/DIPY

Complex	Substituents		% Mg	% N	% C	% H
	R	Ar				
Mg.T ₂ .2H ₂ O	CH ₃	C ₆ H ₅	6.53 (6.67)	23.1 (23.3)	46.48 (46.7)	5.1 (5.6)
Mg.T ₂ .2H ₂ O	C ₆ H ₅	C ₆ H ₅	4.7 (4.96)	17.13 (17.35)	59.12 (59.5)	4.61 (4.95)
Mg.T ₂ . <i>o</i> -phen	CH ₃	C ₆ H ₅	4.52 (4.76)	21.98 (22.22)	61.69 (61.90)	4.37 (4.76)
Mg.T ₂ .dipy	CH ₃	C ₆ H ₅	4.85 (5.0)	23.01 (23.33)	59.73 (60.0)	4.78 (5.0)
Mg.T ₂ . <i>o</i> -phen	C ₆ H ₅	C ₆ H ₅	3.61 (3.82)	17.59 (17.83)	68.31 (68.78)	2.58 (2.86)
Mg.T ₂ .dipy	C ₆ H ₅	C ₆ H ₅	3.79 (3.97)	18.31 (18.54)	67.33 (67.54)	2.61 (2.98)

Values in parentheses indicate calculated ones.

TABLE 2
I.R. BANDS OF TH, Mg.T₂.2H₂O AND Mg.T₂.*o*-phen/dipy in cm⁻¹

Compound	Substituents		ν_{N^3-H}	$\nu_{N \rightarrow O}$	ν_{H_2O}	$\nu_{o\text{-phen/Dipy}}$
	R	Ar				
TH	CH ₃	C ₆ H ₅	3200 s	1300 s	—	—
TH	C ₆ H ₅	C ₆ H ₅	3190 s	1295 s	—	—
Mg.T ₂ .2H ₂ O	CH ₃	C ₆ H ₅	—	1245 s	3400 b	—
Mg.T ₂ .2H ₂ O	C ₆ H ₅	C ₆ H ₅	—	1240 s	3400 b	—
Mg.T ₂ . <i>o</i> -phen	CH ₃	C ₆ H ₅	—	1240 s	—	730 m 1170 m 1420 m
Mg.T ₂ .dipy	CH ₃	C ₆ H ₅	—	1240 s	—	„
Mg.T ₂ . <i>o</i> -phen	C ₆ H ₅	C ₆ H ₅	—	1240 s	—	„
Mg.T ₂ .dipy	C ₆ H ₅	C ₆ H ₅	—	1245 s	—	„

s = strong; m = medium; b = broad.

Magnesium(II) chelates formulated as $\text{MgT}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgT}_2 \cdot o\text{-phen/dipy}$ is supported by analytical data, the non-conductance values and the monomer molecular weights. Further support to above formulations is lent through i.r. studies in the range $4000\text{--}200\text{ cm}^{-1}$ in CsI discs. A broad band at 3400 cm^{-1} indicates the stretch of hydrogen-bonded H_2O molecule, $\overset{3}{\text{N}}\text{-H}$ band at 3200 cm^{-1} of the free ligand disappears after coordination indicating $\overset{3}{\text{N}}\text{-M}$ band and $\overset{1}{\text{N}} \rightarrow \text{O} \rightarrow \text{M}$ electron drainage^{5,6}. Characteristic bands of coordinated *o*-phen/dipy at 730 cm^{-1} , 1170 cm^{-1} , 1420 cm^{-1} also appear in $\text{Mg} \cdot \text{T}_2 \cdot 0\text{-phen/dipy}$.^{7,8} Thus magnesium(II) gives six coordinate complexes and the stereochemistry appears to be trans-diaquo in the case of $\text{Mg} \cdot \text{T}_2 \cdot 2\text{H}_2\text{O}$ due to appearance of a single broad H_2O band at 3400 cm^{-1} . A *cis*-configuration for the two aquo molecules should have led to the splitting of H_2O stretch.⁷ Since magnesium(II) has a spherically symmetrical core (ionic radius 0.78 \AA) of non-bonding electrons the arrangement of ligands in $\text{MgT}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgT}_2 \cdot o\text{-phen/dipy}$ will generate a six coordinate octahedral geometry.¹⁰

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