

Beryllium (II) Complexes of Triazene-1-Oxides

R. SHARMA,* A. K. THAKUR, S. B. RAI,† AND S. N. CHOUDHARY**

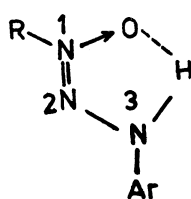
Department of Chemistry

R. D. & D. J. Post Graduate College, Munger-811208, India

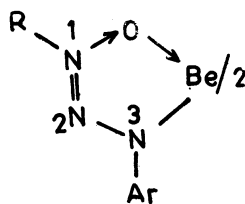
Beryllium (II) complexes of triazene-1-oxides were synthesised and characterised using elemental analyses, conductance, molecular complexities in freezing benzene and IR spectral studies. The complexes obtained were invariable four coordinate and the stereochemistry tetrahedral due to its ionic size and availability of bonding orbitals. Several recrystallisations from acetone gave consistent characterisation data proving that the beryllium complexes obtained were definite molecular addition compounds rather than loose adducts.

INTRODUCTION

Coordination compounds of triazene-1-oxides have recently been reviewed.¹ The present communication describes the syntheses and characterisation of six beryllium (II) complexes of variedly substituted monobasic triazene-1-oxides (TH) represented by general structure 1 and the beryllium (II) complexes by structure 2. The substituents are represented by o-, m-, and p- and are counted from N—C (Ar) bond.



(I)



(II)

EXPERIMENTAL

Ligands were synthesized by following published procedures,² i.e. by coupling substituted hydroxylamine with benzene diazonium chloride at 0–5°C using sodium acetate to control pH. The crude product was recrystallised from ethanol or aqueous-ethanol.

Beryllium (II) complexes of triazene-1-oxides were obtained by two different methods.

† Department of Chemistry, Koshi College, Khagaria.

** Department of Chemistry, J. R. S. College, Jamalpur (Munger).

- (a) Basic beryllium carbonate (3g) suspended in water (40 ml) was converted to the chloride by gradual addition of 6 N-hydrochloric acid (20 ml). The suspension was heated and stirred to yield beryllium chloride (0.05 mol). To this solution an alcoholic solution of triazene-1-oxides (0.1 mol) was added and the solution mixture refluxed for 1 hr. On concentration and cooling crystals of beryllium complexes separated out.
- (b) To hot beryllium chloride solution, ammonium hydroxide solution (in presence of ammonium chloride) was added gradually with stirring till slightly alkaline. The resulting gelatinous precipitate of beryllium hydroxide was washed with water and then refluxed with an alcoholic solution of triazene-1-oxides (0.1 mol) till the hydroxide dissolved. The solution was filtered, concentrated and cooled to yield crystals of beryllium(II) chelates.

Beryllium(II) chelates obtained by both the methods were recrystallised from minimum volume of benzene and reprecipitated by the addition of petroleum-ether with stirring. The yield and the size of crystals of beryllium(II) chelates obtained from the second method were better than the first one. It appears that the higher pH of beryllium chloride solution lowers the yield of the product.

Beryllium was determined as oxide³ and nitrogen by the method of Dumas. C, H were determined at I.I.T., Delhi. Conductivity measurements were made in nitromethane using a Philips conductance bridge and molecular weights were determined in freezing benzene. IR spectra (CsI) were recorded at C.D.R.I., Lucknow.

RESULTS AND DISCUSSIONS

Beryllium(II) chelates of triazene-1-oxides obtained are of the type MT_2 (Table 1). The chelates are neutral and monomer. IR spectra indicate the bonding through both $\overset{3}{N} - \text{atom}$ and $\overset{1}{N} \rightarrow O - \text{atom}$ (Table 2). Beryllium(II), owing to its small size and high charge to radius ratio has the highest polarising power among group IIA metals and is, thus, the most complex former in the group. Beryllium(II) belongs to class (A) acceptor and, therefore, forms strong bonds with oxygen donors. Many four coordinate complexes of beryllium(II) with oxygen and nitrogen donors have been reported.⁴ The limitation for beryllium(II) to give four coordinate complexes involving sp^3 hybrid orbitals is due to non-availability of d-orbitals. The analytical data, the non-conductance values and the monomer molecular weights for beryllium(II) chelates of triazene-1-oxides indicate the bonding of beryllium(II) ion through both $\overset{3}{N} - \text{atom}$ and $\overset{1}{N} \rightarrow O - \text{atom}$. This formulation is further supported by the IR

TABLE 1
ANALYTICAL DATA OF BERYLLIUM(II) CHELATES OF
TRIAZENE-1-OXIDES (TH)

Complex	Substituents		Analysis % : Found / (calcd.)			
	R	Ar	Be	N	C	H
BeT ₂	CH ₃	C ₆ H ₅	2.80 (2.91)	13.62 (13.54)	26.8 (27.18)	2.30 (2.59)
BeT ₂	C ₆ H ₅	C ₆ H ₅	2.72 (2.80)	9.36 (9.70)	32.91 (33.26)	2.20 (2.31)
BeT ₂	CH ₃	C ₆ H ₄ NO ₂ (p)	2.19 (2.26)	14.22 (14.40)	20.80 (21.05)	1.60 (1.75)
BeT ₂	C ₆ H ₅	C ₆ H ₄ NO ₂ (p)	1.63 (1.75)	10.43 (10.71)	27.13 (27.53)	1.58 (1.72)
BeT ₂	CH ₃	C ₆ H ₄ CH ₃ (p)	2.52 (2.67)	12.47 (12.64)	28.03 (28.49)	2.78 (2.97)
BeT ₂	C ₆ H ₅	C ₆ H ₄ CH ₃ (p)	1.79 (1.95)	8.87 (9.11)	33.40 (33.84)	2.20 (2.10)

TABLE 2
IR BANDS OF BeT₂

Compound	Substituents		$\nu \text{N} - \text{H}$ Cm^{-1}	$\nu \text{N} \rightarrow \text{O}$ Cm^{-1}
	R	Ar		
TH	CH ₃	C ₆ H ₅	3200 s	1300 m
TH	C ₆ H ₅	C ₆ H ₅	3200 s	1290 m
BeT ₂	CH ₃	C ₆ H ₅	—	1260 s
BeT ₂	C ₆ H ₅	C ₆ H ₅	—	1253 s

s = strong, m=medium

spectral data. $\nu \text{N}^3 - \text{H}$ band at 3200 cm^{-1} in the free ligand disappears after coordination indicating $\text{N}^3 - \text{M}$ band, and $\nu \text{N}^1 \rightarrow \text{O}$ band at 1300 cm^{-1} is lowered considerably to 1260 cm^{-1} indicating the $\text{N}^1 \rightarrow \text{O} \rightarrow \text{M}$ electron drainage^{5,6}. Thus BeT₂ is four-coordinate and the stereochemistry is tetrahedral involving sp^3 - hybrid orbitals.

REFERENCES

1. R. L. Dutta and R. Sharma. *J. Scient. Ind. Res.*, **40**, 715 (1981).
2. M. Elkins and L. Hunter, *J. Chem. Soc.*, 1346 (1938).
3. A.I. Vogel, *A Text Book of Inorganic Quantitative Analysis*, Longmans Green and Co., p. 578 (1964).
4. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley and Sons, p. 212 (1972).
5. R. L. Dutta and R. Sharma, *J. Indian Chem. Soc.*, **57**, 550 (1980).
6. R. L. Dutta and R. Sharma, *J. Inorg. Nucl. Chem.*, **42**, 1204 (1980).

(Received : 27 May 1991; Accepted : 22 February 1992)

AJC-401