

increasing time. Hence the condition for sustained chain reaction with critical size of the specimen is,

$$\left[\frac{5\pi^2}{a^2} + \frac{\pi^2}{h^2} \right] = B^2 \quad (13)$$

where B is the material buckling given by

$$B^2 = [(k_c - 1)v] / \lambda D \quad (14)$$

The condition (13) leads to the critical volume of the prism, with isosceles right triangular base, as

$$V_{\min} = 201.5 / B^3 \quad (15)$$

The corresponding V_{\min} values for different geometries are given in table 1.

CONCLUSION

The study of diffusion of neutron through a prismatic solid of isosceles right triangular cross-section leads to the important result that this structure is useful for storage of the fissionable material as the minimum critical size is the highest in this case. Further, as the symmetry of the structure decreases the minimum critical size increases.

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TABLE 1

Minimum critical volume for different geometrics

Geometry of the solid	Minimum critical volume (B^3)
Sphere	130
Circular cylinder	148
Cube	161
Prism with equilateral triangular cross-section	186
Prism with isosceles right triangular cross-section	201.5

Chancellor, Marathwada University for his encouragement.

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BINUCLEAR ORGANOSILICON IMINE COMPLEXES, WITH SULPHUR DONOR BENZOTHIAZOLINE

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ABSTRACT

The condensation of salicylaldehyde with *o*-aminobenzenethiol involves the undesirable side reaction resulting in the ring closure with the formation of heterocyclic compound (benzothiazoline). It, however, appears to be in equilibrium with Schiff base form in solution. On reacting trimethylsilyl oxy-metal/non-metal isopropoxides with the ligand in the presence of cyclohexane, the anil form appears to react with isopropoxides and the equilibrium is shifted towards the formation of Schiff base complexes of these metals/non-metals. The resulting new derivatives having M—O—M' bonds have been characterized by elemental analyses, molecular weight determinations, conductance measurements and I.R., U.V. and PMR spectral studies.

INTRODUCTION

METAL chelation is involved in many important biological processes¹ and generally, the chelating ligands are polyfunctional molecules. Recently, much interest has been shown in the synthesis of metal chelates of sulphur containing ligands and it is within this particular area that rather

significant advances have been made². Studies pertaining to M—O—M' bonded imine complexes particularly with sulphur donor ligands are rather scanty. It was, therefore, considered of interest to prepare such types of complexes and the synthesis of complexes of the type, $\text{Me}_3\text{Si-O-M}_1(\text{ONS})$, $\text{Me}_3\text{Si-O-M}_2(\text{OPr}')_n(\text{ONS})$ and $\text{Me}_3\text{Si-O-M}_3(\text{ONS})_2$ [where $M_1 = \text{B(III), Al(III), La(III) and Sm(III)}$; $M_2 =$

Ti(IV), Zr(IV) and Nb (V) when $n=1$ and $M_3=Nb(V)$ when $n=2$ and $ONSH_2 = N-(2\text{-mercaptophenyl})\text{salicylaldehyde}$] are reported in this paper.

EXPERIMENTAL

All the chemicals used were of analytical grade and the reactions were carried out under rigorously anhydrous conditions. Trimethylsilyl acetate (B. P. $103^\circ\text{C}/740\text{ mm}$) was obtained by the reaction between anhydrous sodium acetate and trimethyl chlorosilane in ether (Found: OAc 44.35; Calc.: for $\text{Me}_3\text{SiCO}_2\text{Me}$; OAc 44.71%). Isopropoxides of boron, aluminium, lanthanum, samarium, titanium, zirconium and niobium and the ligand $ONSH_2$ were prepared by the methods reported elsewhere³⁻⁵.

Synthesis of the binuclear complexes

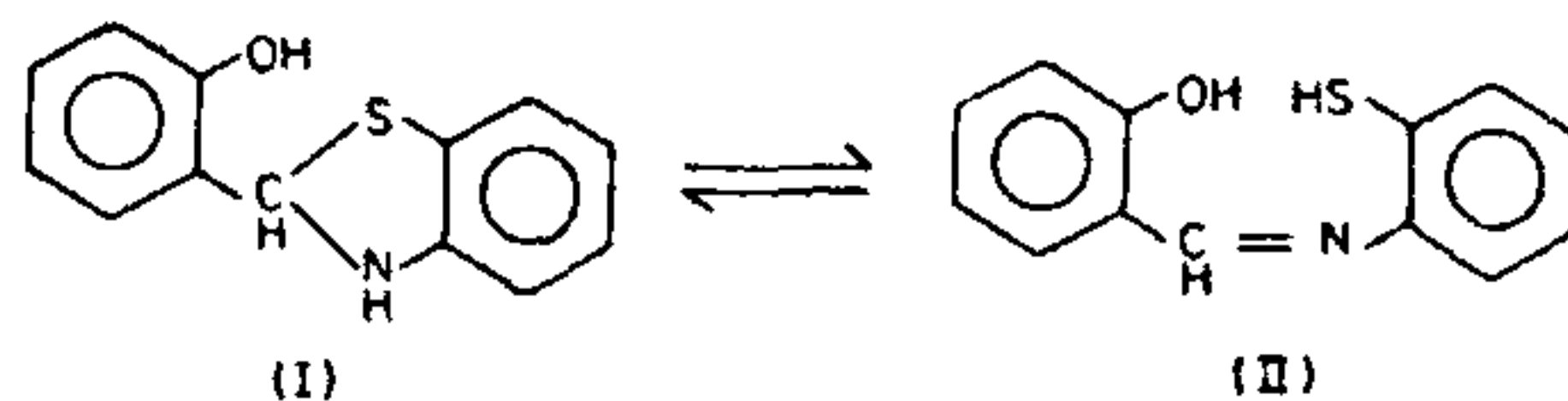
The unimolar reactions between $\text{B}(\text{OPr}^1)_3$, $\text{Al}(\text{OPr}^1)_3$, $\text{La}(\text{OPr}^1)_3$, $\text{Sm}(\text{OPr}^1)_3$, $\text{Zr}(\text{OPr}^1)_4$, Pr^1OH or $\text{Nb}(\text{OPr}^1)_5$ and trimethylsilyl acetate were carried out in dry benzene/cyclohexane medium. The isopropoxide was refluxed under a fractionating column and the calculated amount of the trimethylsilyl acetate diluted with benzene/cyclohexane was added dropwise with a dropping funnel. The isopropyl acetate liberated during the course of the reaction was continuously fractionated off azeotropically with benzene/cyclohexane (8-10 hr). To the resulting products, an equimolar amount of $ONSH_2$ [bimolar only in the case of $\text{Nb}(V)$ complex] was added. The reaction mixture was further refluxed and the isopropanol liberated was fractionated out along with the benzene, till the reaction was complete (12-14 hr). The liberation of almost theoretical amount of isopropanol in the azeotrope confirmed the completion of the desired reaction. The excess of the solvent was then removed by distillation and the last traces of the volatile material were removed under reduced pressure. The solid products so obtained (yield $\sim 87\%$) were identified and then characterized.

RESULTS AND DISCUSSION

The spectral studies and conductance measurements of the resulting bimetallic complexes show the formation of $\text{Me}_3\text{Si-O-B}(\text{ONS})$, $\text{Me}_3\text{Si-O-Al}(\text{ONS})$, $\text{Me}_3\text{Si-O-La}(\text{ONS})$, $\text{Me}_3\text{Si-O-Sm}(\text{ONS})$, $\text{Me}_3\text{Si-O-Ti}(\text{OPr}^1)(\text{ONS})$, $\text{Me}_3\text{Si-O-Zr}(\text{OPr}^1)(\text{ONS})$, $\text{Me}_3\text{Si-O-Nb}(\text{OPr}^1)_2(\text{ONS})$ and $\text{Me}_3\text{Si-O-Nb}(\text{ONS})_2$ type of complexes. These are obtained as coloured solids and found to be soluble in chloroform, DMF and DMSO.

The absence of ν_{SH} band in the region, 2600-2500 cm^{-1} and the appearance of a strong and sharp ν_{NH} band in the region, 3400-3260 cm^{-1} in the ligand is a

strong evidence for the existence of benzothiazoline structure (I) and not the imine structure (II) of the ligand. However, a broadening in this band in the ligand, $ONSH_2$ indicates the probable association of ν_{NH} with the phenolic ν_{OH} vibrations.



The disappearance of this band in the IR spectra of metal complexes shows the chelation of oxygen as well as nitrogen of the ligand to the central metal atom. Further, in the case of metal complexes, a strong band around 1600 cm^{-1} (table 1) may be ascribed to the coordinated $>\text{C}=\text{N}$ group⁶ and this very well supports the fact that the resulting complexes are metal-imine derivatives, as the benzothiazoline ring rearranges to give the imine, which finally acts as a bibasic tridentate ligand.

The appearance of several new bands of strong to medium intensity in the regions, 700-510 and 1335, 560-400 and 1545 and 400-290 cm^{-1} are due to the metal-oxygen, metal-nitrogen and metal-sulphur stretching vibrations respectively. A band of medium intensity at $\sim 1250\text{ cm}^{-1}$ in the complexes is the characteristic band of the $-\text{SiMe}_3$ group.

The electronic spectrum of the ligand shows two bands at 250 and 310 nm and these are fully consistent with the typical spectrum of benzothiazolines⁷. These bands arising out of $\phi-\phi^*$ and $\pi-\pi^*$ benzenoid⁸ transitions remain unaltered in all the metal complexes, whereas an additional band is also observed at $\sim 415\text{ nm}$ due to $n-\pi^*$ electronic transitions of the azomethine group^{9,10} indicating the isomerization of the ligand on complexation.

The coordination of metal to nitrogen, oxygen and sulphur atoms is further supported by a comparison of the ^1H nmr spectral data of the ligand $ONSH_2$ and its complex, $\text{Me}_3\text{Si-O-B}(\text{ONS})$. The ^1H nmr spectrum of the ligand shows the OH and NH proton signals at δ 9.25 and 5.65 ppm respectively. However, in the complexes, these signals disappear showing the chelation through the functional groups. Further, the sharp singlet due to the azomethine proton at δ 8.60 ppm in the ligand shifts downfield (δ 9.0 ppm) in the spectrum of the complex, showing the coordination of azomethine nitrogen to the metal atoms.

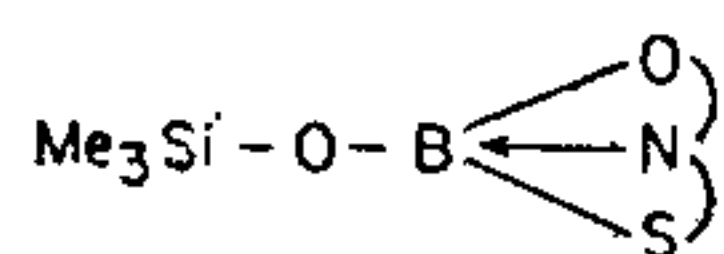
The molecular weight determinations in boiling chloroform show the monomeric nature of the resulting complexes. It may thus be concluded that in all the resulting complexes the silicon is in the tetracoordinated environment, whereas the second

TABLE I
Physical properties and IR spectral data of the binuclear complexes

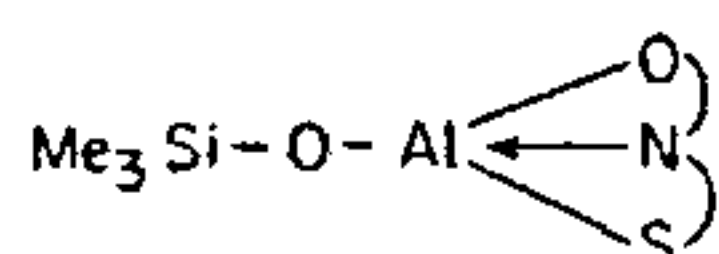
Compound	Colour	M.P. (°C)	Mol. Wt. Found (Calc.) ^a	ν_{C-N}	ν_{M-O}	ν_{M-N}	ν_{M-S}
Me ₃ Si-O-B (ONS)	Brownish yellow	105-06	340 (328)	1610vs	1335m	1545m	800w
Me ₃ Si-O-Al (ONS)	Yellow	195-97	355 (343)	1620vs	630 s	490m	330m
Me ₃ Si-O-La (ONS)	Dark yellow	224-25	470 (455)	1580vs	705 s	400m	320m
Me ₃ Si-O-Sm (ONS)	Dark yellow	202-03	485 (466)	1590vs	645m	430w	340w
Me ₃ Si-O-Ti(OPr ⁱ) (ONS)	Dark brown	185-86	420 (423)	1600vs	615m	490m	330m
Me ₃ Si-O-Zr(OPr ⁱ) (ONS)	Orange	210-11	459 (466)	1590vs	600 s	500m	350w
Me ₃ Si-O-Nb(OPr ⁱ) ₂ (ONS)	Dull red	146-47	539 (527)	1590vs	635 s	435w	340w
Me ₃ Si-O-Nb(ONS) ₂	Light red	162-63d	654 (636)	1595vs	600 s	420m	330w

ONS = C₁₃ H₉ NOS; VS = very strong, s = strong, m = medium and w = weak

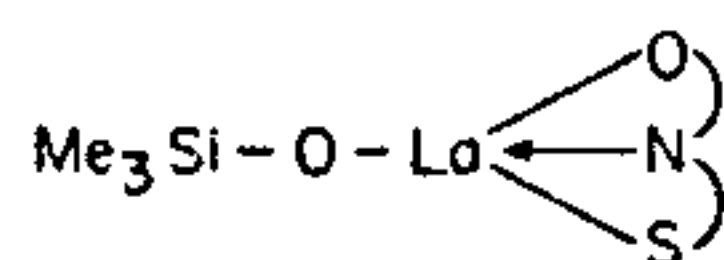
non-metallic/metallic centre is tetracoordinated, in III, IV, V and VI penta-coordinated in VII and VIII and hexa- and hepta-coordinated in IX and X type of binuclear derivatives.



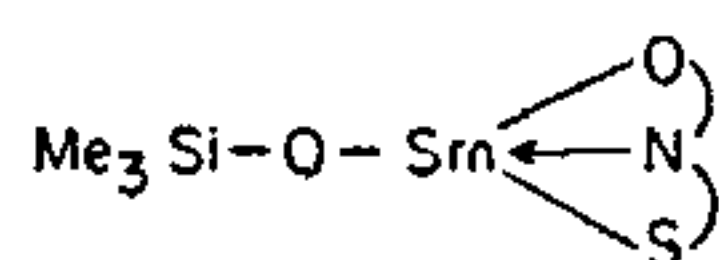
III



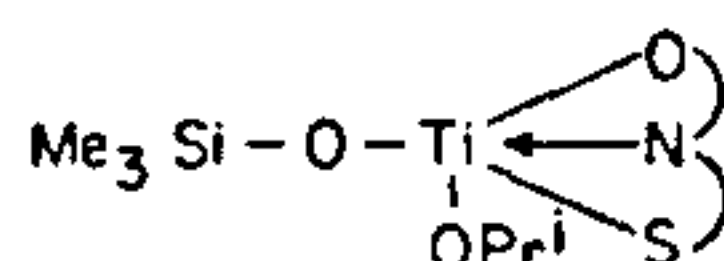
VI



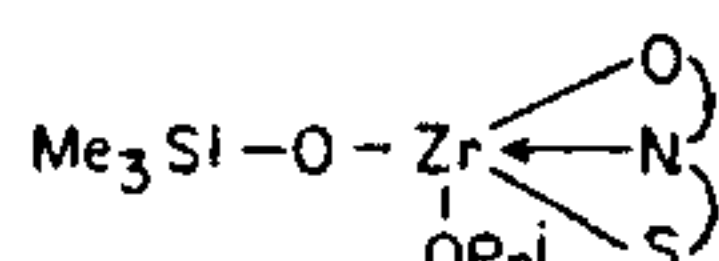
V



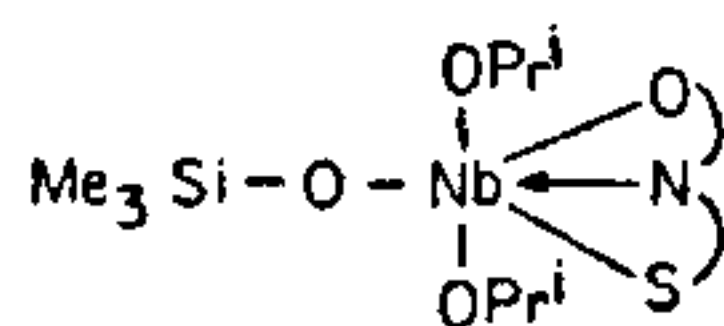
IV



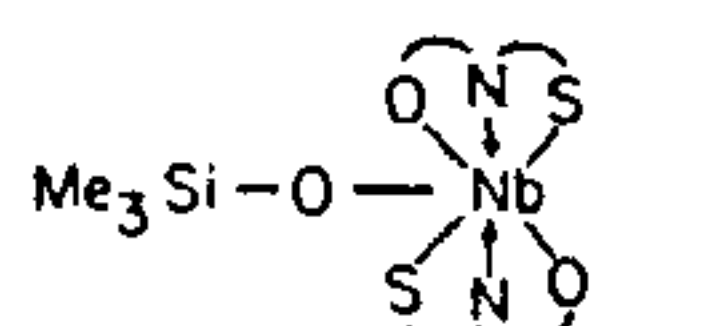
VII



VIII



IX



X

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