

Structural aspects of some modified metal-alkoxides and related molecular precursors to ceramic materials by the sol-gel processing^ψ

Rakesh Bohra

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

E-mail : rkbohra@satyam.net.in

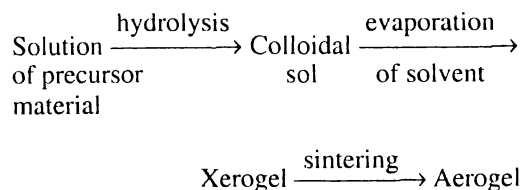
There is an increasing interest in designing better modified metal-alkoxide precursors for the deposition of metal-oxides and organic-inorganic hybrid materials by sol-gel/MOCVD techniques. In the alkoxide based sol-gel processes, gelation occurs through the development of a polymeric network formed as a consequence of the initial hydrolysis of the metal-alkoxides in the presence of water and its subsequent polymerization by condensation mechanism. Modifiers such as β -diketones, carboxylic acids, Schiff's bases, glycols etc. can modify the relative reaction rates (by chelation effect) providing a better route to the formation of the gelatinous precipitate required for ceramic material applications. Such organically modified metal-alkoxides and related precursors also allow the introduction of organic moieties for organic-inorganic hybrid material applications.

Considerable amount of research work has been reported from our laboratories on various synthetic and structural aspects of derivatives containing M-O-C, M-S-C and M-N-C functionalities during the last three decades, yet much of the later developments coincided with the synthesis and characterization of the modified precursors for material applications. The present article deals with the synthesis and structural aspects of some modified metal-alkoxides and related precursors of some main group p-block and early d-block elements having potential applications in material science.

Introduction

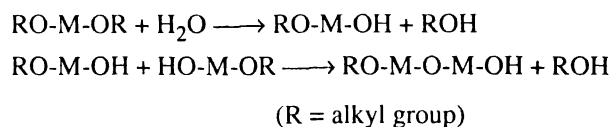
Chemically modified metal-alkoxides and related derivatives play an important role as precursors to ceramic materials by sol-gel processing or metal-organic chemical vapour deposition technique. This has resulted in an intense activity in the field of nano-technology, an area of current interest due to the dramatic change in material properties at nanometer scale. The solution based sol-gel technology has been employed extensively in the production of high quality (amorphous or crystalline) oxide ceramics at low temperature with specified mechanical, optical, electronic and physicochemical properties in a variety of shapes from powders to fibers including deposition of thin films on various substrates. Applying the sol-gel process, it is also feasible to control the entire synthetic route from precursor to the final targeted material at the molecular level, which is unachievable with traditional sintering or precipitation methods.

An understanding of the sol-gel path involves an understanding of the reactions and processes occurring at the molecular level. A most simplified sol-gel process involves the following basic steps :



In the beginning these aerogels were prepared using inorganic precursors (e.g. metal salts) requiring long gelation time and high sintering temperatures¹. However, the use of metallo-organic precursors, mainly the metal(heterometal)-alkoxides²⁻⁴ gave a major breakthrough to this technology because of the various advantages over the traditional methods including uniformity in processing, control over the stoichiometry, reduced sintering temperatures and the formation of volatile side products.

In the alkoxide based sol-gel processes, gelation occurs through the development of a polymeric network formed as a consequence of the reactions of the following types :



^ψAcharya P. C. Ray Memorial Lecture (2003) delivered under the auspices of Indian Chemical Society on 24 December 2004 at Delhi, India.

Once the hydrolysis is initiated the above reactions occur simultaneously. The nature of the resultant network structure would depend on the relative kinetics of (i) the initial hydrolysis of the metal-alkoxides in the presence of water and (ii) its subsequent polymerization by condensation mechanism. A polymeric gel is obtained if the hydrolysis reaction is much faster than the polymerization by condensation mechanism. On the other hand, a gelatinous precipitate or a colloidal gel is obtained when the kinetics of the above two reactions are fast enough and become similar. Modifiers such as β -diketonates, glycols etc. can modify the reaction kinetics by chelation effect³. It appears that the resultant steric hindrance by anisotropic growth of oligomers inhibits the rapid hydrolysis that causes the formation of the polymeric gels.

A great deal of research work on various synthetic and structural aspects on derivatives containing M-O-C, M-S-C and M-N-C functionalities has been reported from our as well as other laboratories⁵⁻¹³. The initial aim of synthesizing the metal-alkoxides and related derivatives was to prepare a wide variety of compounds of empirical formula $L_xM(OR)_y$ (where R is an alkyl group, L a neutral or anionic ligand and x and y are integers), the synthesis of which may not be possible by any other route in the required high purity. But much of the later developments in this field coincided with an interest in designing better precursors for the deposition of metal oxides and organic-inorganic hybrid materials by methods such as the sol-gel or MOCVD.

Therefore, the current research interest is on the synthesis and characterization of tailor made precursors of these alkoxides prepared by the partial replacement of alkoxo groups with less hydrolysable groups such as oxo-, β -diketonates, carboxylates and many other chelating or non-chelating modifiers, which tend to lower their rate of hydrolysis^{2-4,12,13}. Furthermore, such organically modified metal alkoxides and related precursors allows the introduction of organic moieties for organic-inorganic hybrid material applications¹⁴⁻¹⁶. Syntheses of these materials require that the oxide cluster and organic compound should be soluble in a common organic solvent and a bond formation should be there to maintain a compatible single phase.

The present article deals with the synthesis and structural aspects of some modified metal-alkoxides and related precursors of some main group p-block and early d-block elements having potential applications in material science.

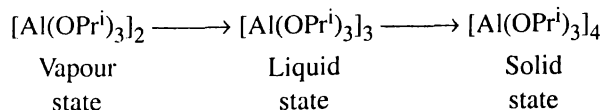
Group 13 metalloorganics

Group 13 elements find a special place in the field of

semiconductor devices¹⁶. Metalloorganic compounds featuring bonds between group 13 and 15 elements^{17,18} and between 13 and 16 elements¹⁹⁻²³ have interest due to their applications as precursors for MOCVD and sol-gel preparation of the desired materials.

Aluminium alkoxides and oxoalkoxides are rich with the accessibility of the soluble forms, oligomeric characteristics, interesting coordination chemistry and geometries and most importantly the ease of hydrolysis, a property increasingly exploited for the low temperature synthesis of oxide ceramics by sol-gel process^{13,20,21,23}.

Amongst aluminium-alkoxides, the chemistry of aluminium-isopropoxides received considerable attention. It had been reported to depict varying degree of molecular association, e.g. 2- >4. On this aspect, a conceptual approach was directed by Mehrotra²⁴, using the phenomenon of "ageing" as depicted below :



Existence of tetrameric structure in solution has been confirmed by ¹H and ²⁷Al NMR spectral studies^{25,26}. The ²⁷Al NMR spectrum in toluene exhibits two sets of signals at δ 1.72 ppm and δ 65.0 ppm in the range of six- and four-coordinated Al^{III} atoms, respectively. This inference got further support by the solid state single crystal X-ray diffraction study of $[Al(OPr^i)_3]_4$ ²⁷.

It has been shown that the decrease in electronegativity of the bridging group between two metal centers results in increase in 'Metal-Metal' repulsions in dimeric systems. Probably because of this reason, the thio analogues of organoaluminium alkoxides, which are dimeric in the gaseous state becomes polymeric in the solid state with large Metal-Metal distances²⁸.

Due to the high susceptibility of aluminium-alkoxides, a control on the hydrolysis rate was achieved by the use of chemical modifiers. In this regard partially substituted aluminium-alkoxide- β -diketonate complexes provided very interesting considerations towards structural aspects as well as their activity as catalysts and as ceramic precursors²⁹. Complexes of the formula $[Al(OR)_2(\beta\text{-diketonate})]_2$ exist as asymmetric dinuclear complexes (when R = OPrⁱ, OSiMe₃, t-Bu) containing tetrahedral and octahedral Al sites, on a two fold-axis (Fig. 1).

Prolonged standing of the compound $[Al(OPr^i)_2(acac)]_2$ in solution at room temperature yields a white crystalline

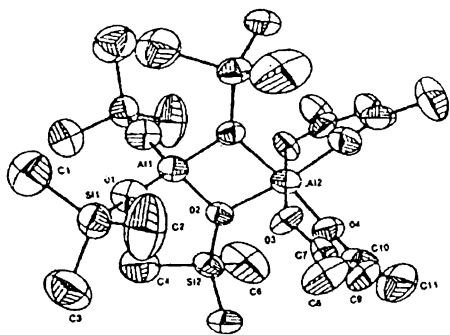
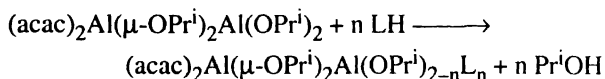


Fig. 1. Crystal structure of $[\text{Al}(\text{OSiMe}_3)_2(\text{acac})]_2$.

solid $[\text{Al}(\text{OPr}^i)_2(\text{acac})]_3$. X-Ray diffraction study reveals an interesting distribution of ligand moieties on the three aluminium atoms. Two octahedral Al atoms are bonded with two and one acetylacetonate moieties, respectively, while the third tetrahedral Al atom is bonded with two terminal and two bridging isopropoxy moieties. However, the use of highly sterically crowded triphenylsilanol, in place of isopropanol resulted in the formation of four-coordinated monomers. With smaller alkoxo-ligands like methoxy, a polymeric white flocculent solid was obtained.

Complexes of the formula $[\text{Al}(\text{OR})(\beta\text{-diketonate})_2]$ are dimeric with the possibilities of existence of stereoisomers, which is reflected in their NMR spectra. Crystal structure analysis $[\text{Al}(\text{OPr}^i)(\text{Et}_2\text{acac})_2]_2$ demonstrate steric crowding around both the octahedral Al atoms. It is interesting to mention here that the aluminiumtris(β -diketonate) complexes are monomeric with hexa-coordinated Al center³⁰. These studies do indicate that chelating ligands reduce the Lewis acidity of the resulting complexes.

Systematic studies on some novel heterocyclic derivatives containing aluminium(III) atoms in different coordination states have been recently reported from our laboratories using the reactions of the following type :



(where $n = 1$ or 2 ; when LH is a monofunctional ligand like 8-hydroxyquinoline³¹, oximes³², triphenylsilanol³³, *O*-aminobenzoic acid³⁴, 2-pyridylmethanol³⁵, amino alcohols³⁶, Schiff's bases³⁷ and $n = 1$, when LH is a bi-functional ligand like mercaptoalcohol³⁸, glycols³⁹ etc.).

In addition to the above, some bridged glycolate complexes of aluminium(III) have also been prepared by the reaction of $(\text{acac})_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2$ with glycol in 1 : 2 molar ratio in anhydrous benzene⁴⁰.

All these dinuclear derivatives, $(\text{acac})_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_{2-n}\text{L}_n$, have been characterized by elemental analysis and spectroscopic (IR and multinuclear NMR) studies. ^{27}Al NMR spectral studies appear to be the most important tool for structural characterization of aluminium(III) derivatives. The range of ^{27}Al NMR chemical shifts of all these complexes indicate the presence of Al^{III} atoms in different coordination states (Fig. 2a). Following general structure may be proposed for these derivatives (Fig. 2b). It appears that the introduction of organic functionalities might play a significant role in modifying

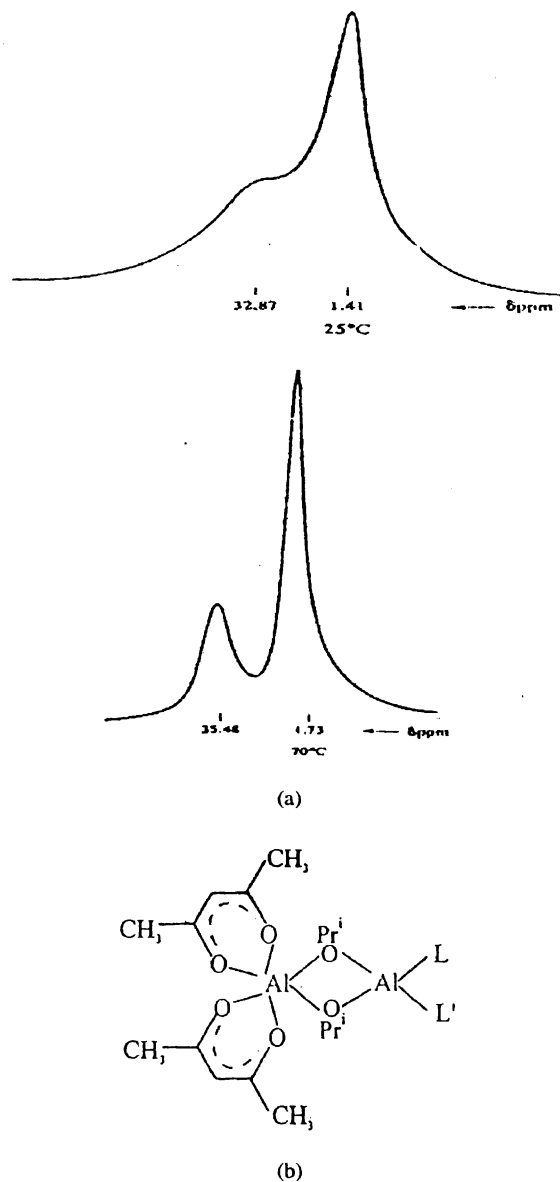
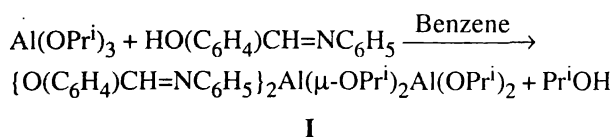


Fig. 2. (a) ^{27}Al NMR spectrum of a representative complex^{39a}
(b) Proposed structure for $(\text{acac})_2\text{Al}(\mu\text{-OPr})_2\text{AlILL}'$.

the solubility and reactivity of the resulting alkoxide derivatives to make them better precursors for high-purity metal-oxide based ceramic materials.

It is worthwhile to mention here that the corresponding boron analogous, $[(\beta\text{-diketonate})\text{B}(\text{OPr}^i)_2]$ are monomeric and their further reaction with a variety of glycols in anhydrous benzene resulted in the formation of tetra-coordinated boron(III) complexes^{41,42}. In the ^{11}B NMR spectra of these derivatives, the presence of two set of resonances with unequal intensity indicate the existence of equilibrium between tri- and tetra-coordinated structures.

The studies on a wide variety of compounds of aluminium(III) exhibiting unsymmetrical structures, indicate that the steric and electronic factors play a very important role in aluminium(alkoxo)(β -diketonate) chemistry^{35–40}. Therefore, attempts have also been made to prepare other derivatives using similar chelating ligands. In this context a new heteroleptic precursor, [bis(*N*-phenylsalicylideneiminato)-aluminium-di- μ -isopropoxo-diisopropoxo-aluminium(III)], has been prepared by the reaction of $\text{Al}(\text{OPr}^i)_3$ and *N*-phenylsalicylidene imine in 1 : 1 molar ratio in refluxing anhydrous benzene⁴³.



Compound **I** is obtained in quantitative yield as the sole product without co-existence of any geometrical isomer (Fig. 3). This fact was also confirmed by its ^{27}Al NMR spectra in which only two resonances were observed at δ 7.8 and 40.1 ppm, which were assigned to 6- and 4-coordinated aluminium(III) atoms, respectively. The crystal structure of **I**, exhibits interesting variations in Al-O(alkoxo) bond distances :

- (i) 1.932(3)–1.909(3) Å for Al(hexa-coordinated)-O(bridging),
- (ii) 1.792(3)–1.799(3) Å for Al(tetra-coordinated)-O(bridging), and
- (iii) 1.704(3)–1.685(3) Å for Al(tetra-coordinated)-O(terminal)

Reaction of **I** with alkoxyalkanols in 1 : 1 and 1 : 2 molar ratios in refluxing anhydrous benzene yield alkoxo-bridged complexes of the type $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OR})_n(\text{OPr}^i)_{2-n}$. Multinuclear NMR studies indicate monodentate behaviour of alkoxy-alkanol moieties and retention of 6- and 4-coordination in these binuclear derivatives also.

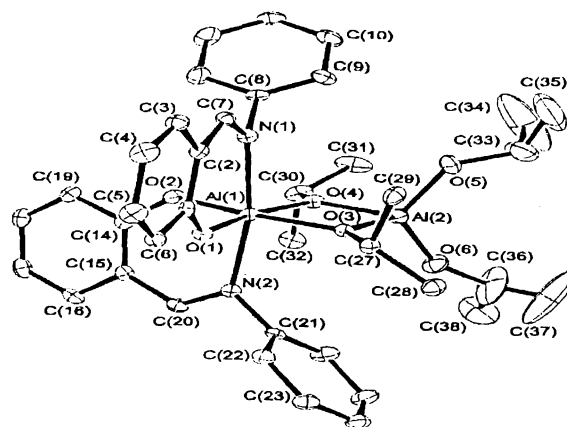


Fig. 3. Crystal structure of $\{\text{O}(\text{C}_6\text{H}_4)\text{CH}=\text{NC}_6\text{H}_5\}_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2$.

Similarly further reaction of **I** with diols yielded terminal chelated-alkoxo-bridged, bis(*N*-phenylsalicylideneiminato)Al^{III} complexes⁴⁴.

As coordination number five appears to be less common in Al^{III} derivatives, therefore preparation of some heteroleptic complexes of Al^{III} with *N*-phenylsalicylideneiminato and internally functionalized oximes in various stoichiometric ratios is quite interesting⁴⁵. Crystal structure analysis of one of the derivatives, $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}[\text{ON}=\text{C}(\text{Me})\text{C}_4\text{H}_3\text{S}-2]$ revealed Al atom in a distorted trigonal bipyramidal environment with all the three oxygen atoms at equatorial positions (Fig. 4). The axial positions are occupied by the nitrogen atoms of the *N*-phenylsalicylideneimine ligand moieties.

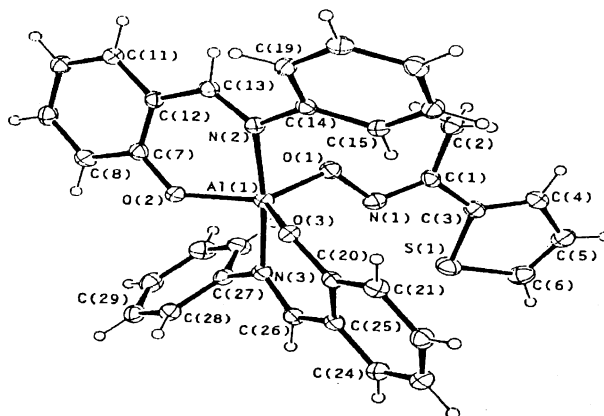


Fig. 4. Crystal structure of $[\text{C}_6\text{H}_4\text{OCH}=\text{NC}_6\text{H}_5]_2\text{Al}[\text{ONC}(\text{Me})\text{C}_4\text{H}_3\text{S}]$.

In view of the above interesting findings, some organoaluminium(III) complexes have also been synthesized

by the reaction of triethylaluminium ethrate adduct ($\text{Et}_3\text{Al} \cdot \text{Et}_2\text{O}$) with a variety of aminoalcohols, which are of special interest due to the presence of both hydroxyl as well as amino groups^{46a}. On the basis of the molecular weight measurements of both the 1 : 1 (dimer) and 1 : 2 (monomer) derivatives and the range of ^{27}Al chemical shifts (δ 67.3–71.2 ppm) exhibited by them, presence of penta-coordination around Al atom was suggested. Similarly, penta-coordination in mono and di-ethylaluminium(III) complexes with internally functionalized oximes has been suggested with the help of ^{27}Al NMR studies^{46b}. Crystal structure analysis of an ionic complex, $[\text{Al}\{\text{C}_6\text{H}_4\text{O}(\text{CH}=\text{NC}_6\text{H}_5)\}_2\{\text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{NC}_6\text{H}_5\}_2]^+\text{Br}^-$, obtained during the reaction of Et_2AlBr with a Schiff's base, on the other hand revealed octahedral environment around aluminium(III) atom (Fig. 5)⁴⁷.

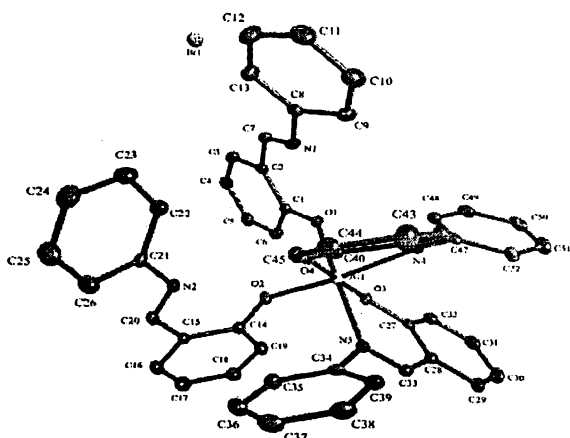


Fig. 5. Crystal and molecular structure of $[\text{Al}\{\text{C}_6\text{H}_4\text{O}(\text{CH}=\text{NC}_6\text{H}_5)\}_2\{\text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{NC}_6\text{H}_5\}_2]^+\text{Br}^-$.

Group 14 metalloorganics and related derivative

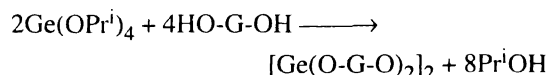
Heavy group 14 elements exhibit most varied coordination chemistry of any similar group of elements in the periodic table. The metalloorganic compounds of these elements find extensive applications in industries because of their catalytic^{48–50} and biological activities^{51,52} as well as their increasing use in material science^{53,54}. Thin films of these M-oxides are widely used as semiconductors and have potential applications in light-emitting diodes, in infrared detectors and in opto-electronic devices.

The involvement of these derivatives in sol-gel technology for the preparation of thin films or nanocomposites of inorganic and hybrid materials is a current thrust area of research because of the low cost of the starting materials^{55,56}. SnO_2 thin films doped with other elements ex-

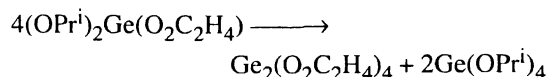
hibit best mechanical, chemical and thermal stabilities and least toxicity⁵⁷.

The alkoxide chemistry of germanium was initiated by Key *et al.*^{58–60} and extended by Mehrotra and co-workers^{61–63}. Generally, germanium compounds are stable in the tetravalent state. However, the stabilization of divalent germanium compounds require sterically demanding ligands.

Recently, we reported⁶⁴ some interesting reactions of $\text{Ge}(\text{OPr}^i)_4$ with glycols to yield dimeric complexes of the following type :



Mixed ligand complexes of the type, $(\text{OPr}^i)_2\text{Ge}(\text{O-G-O})$, have also been prepared and characterized. The compound $(\text{OPr}^i)_2\text{Ge}(\text{O}_2\text{C}_2\text{H}_4)$ exhibits disproportionation reaction :



X-Ray diffraction study of $\text{Ge}_2(\text{O}_2\text{C}_2\text{H}_4)_4$ revealed interesting feature in its bond lengths and bond angles. The four-membered Ge_2O_2 ring is planar (Fig. 6). The Ge-O bonds within the digermanoxane ring differ very much (Ge-O; 1.835 and 2.082 Å). Each oxygen atom of the ring belongs to the bridging and chelating five-membered diolato ligand with envelope conformation. Germanium atoms are in distorted trigonal-bipyramidal configuration. The second diolato-ligand acts only chelating and has a less distorted envelope conformation.

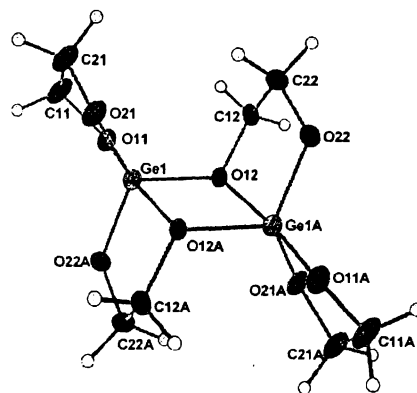


Fig. 6. Crystal structure of $\text{Ge}(\text{OCH}_2\text{CH}_2\text{O})_2$.

When monofunctional ligands having additional donor sites, e.g. alkoxyalkanols, react with $\text{Ge}(\text{OPr}^i)_4$ in various stoichiometries, only tetra-coordinated species of the type

$[\text{Ge}(\text{OCH}_2\text{CH}_2\text{OR})_n(\text{OPr}^i)_{4-n}]$ (where $\text{R} = \text{Me}, \text{Et}$ and Bu ; $n = 1-4$) were obtained⁶⁵. On the basis of the molecular weight measurements and spectroscopic data, a tetrahedral geometry around Ge atom has been proposed. Some volatile tetra-coordinated triorganogermanium(IV) complexes with internally functionalized oximes have also been reported⁶⁶. Spectroscopic data indicate that the heteroatoms of the oximato moiety are not taking part in coordination.

A comparison of the structure of $[\text{Ge}(\text{OCH}_2\text{CH}_2\text{O})_2]_2$ with the related structure of $[\text{TiO}(\text{acac})_2]_2$, revealed that the Ti_2O_2 ring is also planar but symmetrical⁶⁷ (Fig. 7a). In this titanoxane ring the titanium atoms are in somewhat distorted octahedral environment. On the other hand the corresponding $\text{OV}(\beta\text{-diketonate})_2$ is monomeric and exhibits penta-coordination around vanadium atom (Fig. 7b)⁶⁸.

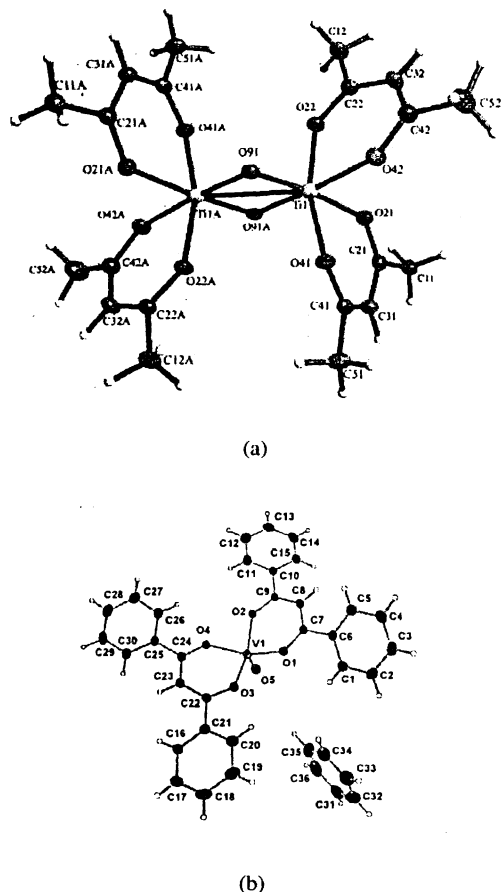


Fig. 7. Crystal structure of (a) $[\text{Ti}(\text{acac})_2\text{O}]_2$ and (b) $\text{OV}(\beta\text{-diketonate})_2$.

A related heteroleptic zirconium derivative, $[(\text{acac})_2\text{Zr}\{\text{ONC}(\text{Me})\text{Py-2}\}_2]$, exhibits the presence of a central zirconium atom in coordination number eight^{69a}. The two acetylacetonato-O,O' ligands are bonded in cisoidal man-

ner and the two oximato ligands are linked in a $\eta^2\text{-N,O}$ fashion to the central zirconium atom (Fig. 8a). Participation of oxime-N in coordination may be due to the increased size of the central atom. Although Zr-N distances are the largest ($\approx 2.24 \text{ \AA}$). The oximato-N atoms lie closer to the trans-axial positions of the oxygen atoms of the acac rings ($\approx 166^\circ$). A similar type of bonding has also been observed in $\text{OV}\{\text{ONC}(\text{Me})\text{C}_4\text{H}_3\text{O-2}\}_3$ (Fig. 8b)⁶⁹.

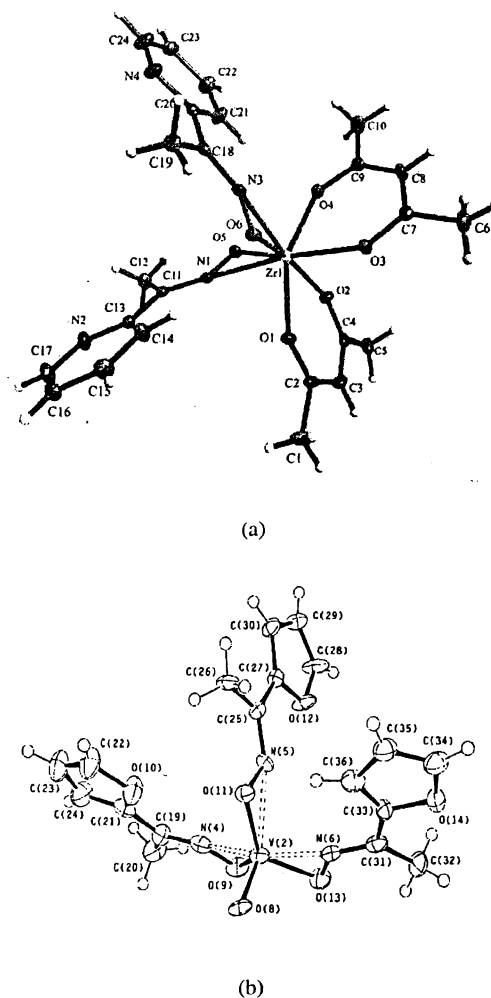
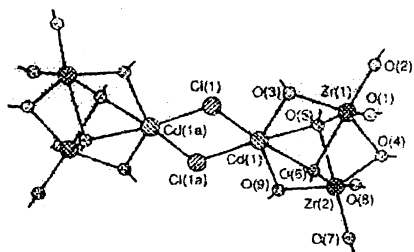
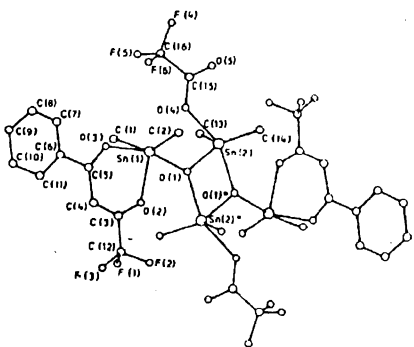


Fig. 8. Crystal structure of (a) $[(\text{acac})_2\text{Zr}\{\text{ONC}(\text{Me})\text{C}_5\text{H}_4\text{N-2}\}_2]$ and (b) $\text{OV}\{\text{ONC}(\text{Me})\text{C}_4\text{H}_3\text{O-2}\}_3$.

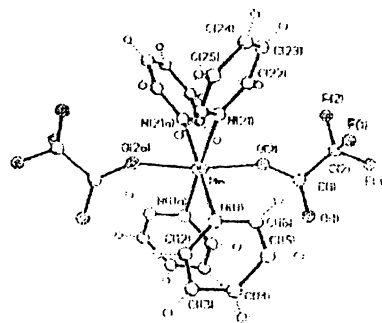
In addition to the above the first (chloro)alkoxo-cadmium-zirconate derivative, $[\{\text{Cd}[\text{Zr}_2(\text{OPr}^i)_9](\mu\text{-Cl})\}_2]$, has also been characterized by X-ray crystallography (Fig. 9) exhibiting interesting structural variations⁷⁰. Such derivatives may be potential candidates for ceramic materials by the sol-gel processing.


 Fig. 9. Crystal structure of $[Cd[Zr_2(OPr)_9](\mu-Cl)_2]$.

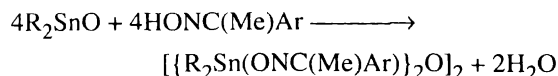
Interest in the chemistry of organotin oxide networks is due to the accessibility of a wide range of structural patterns like drum-shaped, cubic, capped tetrahedron *etc.*^{71,72} and their applications as precursors in material science^{73,74}. In this regard organostannoxanes have received considerable attention because such derivatives may also exhibit a variety of unique structures, e.g. in the structure of unsymmetrical stannoxanes, of the formula $[C_6H_5C(O)CHCO(CF_3)Sn(Me)_2]O[SnMe_2(O_2CCF_3)]_2$, obtained by the condensation reaction of dimethyltin oxide with $C_6H_5COCH_2COCF_3$ and CF_3COOH in 2 : 1 : 1 molar ratio in refluxing benzene, both the exo- as well as the endo-cyclic-tin atoms are penta-coordinated with *thp* geometry and none of the ligand moieties are taking part in bridging the tin atoms^{75a} (which is generally very common in the solid-state structures for such type of compounds^{e.g.} 76,77) (Fig. 10).


 Fig. 10. Crystal structure of $[C_6H_5C(O)CHCO(CF_3)Sn(Me)_2]O[SnMe_2(O_2CCF_3)]_2$.

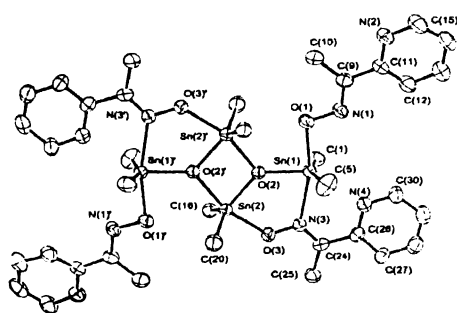
It is interesting to mention here that the reaction of Mn powder with CF_3COOH gave a product $Mn(O_2CCF_3)_2$ **1**. The aggregation of **1** is directed by different N-containing bases. Pyridine (Py), for example, forms^{75b} the mono nuclear complex $[Mn(O_2CCF_3)_2(Py)_4]$ (Fig. 11) and benzonitrile (benz) yields the trinuclear complex $[Mn_3(O_2CCF_3)_6(benz)_6]$.


 Fig. 11. Crystal structure of $[Mn(O_2CCF_3)_2(Py)_4]$.

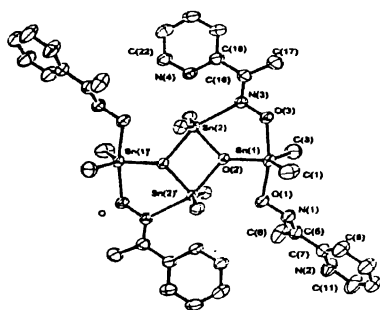
Recently, we reported the syntheses and structures of some novel tetraorganodistannoxanes with internally functionalized oximes^{78,79}. Diorganotin(IV) complexes of the type $[R_2Sn(ON=C(Me)Py-2)]_2O_2$ ($R = Bu^t, Pr^t, Et$ and Me) have been synthesized by condensation reactions and characterized by elemental analysis, IR and NMR (1H , ^{13}C and ^{119}Sn) spectroscopy⁷⁸.



Like ^{27}Al NMR spectroscopy, the ^{119}Sn NMR spectroscopy is also an important tool for the structural elucidations. Two sets of ^{119}Sn chemical shifts are observed in the ^{119}Sn NMR spectra of all these compounds (in the region δ -190.8 to -220.4 and -219.9 to -239.4 ppm) indicating the presence of two types of environment around the tin atoms. These stannoxanes exhibit dynamic behaviour in solution, which is reflected in the 1H and ^{13}C NMR spectra of these complexes. Only a single set of ligand proton and carbon signals had appeared in spite of their different bonding patterns within a stannoxanes frame work. Crystal structure analysis of Bu- and Et-tin derivatives revealed interesting structural variations. In the structure of dibutyl derivative each tin is bonded to the uninegative ligand moiety, which is very similar to the previously reported tetraorganodistannoxane structures (Fig. 12a). However in the case of diethyl derivative (Fig. 12b) each of the exo-cyclic tin atoms is bonded to two oximate anions and the oxime-nitrogen of one of the anions is coordinated to the endo-cyclic tin atoms. Both endo- and exo-cyclic tin atoms in dibutyl- and diethyl-derivatives are in distorted *thp* configurations with the R groups occupying the equatorial positions. The four-membered Sn_2O_2 ring is planar and asymmetrical ($Sn-O$, ≈ 2.048 and ~ 2.19 Å). These molecules adopt a staircase conformation in the solid-state.



(a)



(b)

Fig. 12. Crystal structure of (a) $[\{Bu^n_2Sn(ONC(Me)C_5H_4N-2)\}_2O]_2$ and (b) $[\{Et_2Sn(ONC(Me)C_5H_4N-2)\}_2O]_2$.

Crystal structure analysis of $[\{Me_2Sn(ON=C(Me)Py)\}_2O]_2 \cdot 2[2-Py(Me)C=NOH]$ ⁷⁹, which is a hydrolysis product obtained during the reaction of Me_2SnCl_2 with the sodium salt of the ligand in 1 : 2 molar ratio, revealed two unique characters (Fig. 13); (i) this is the first structural motif in which two free oximes are connected to the stannoxane frame work in this manner, a property which may be of use in the preparation of hybrid materials, and (ii) the four-membered Sn_2O_2 ring is symmetrical. It is interesting to compare the degree of hydrogen bonding in the

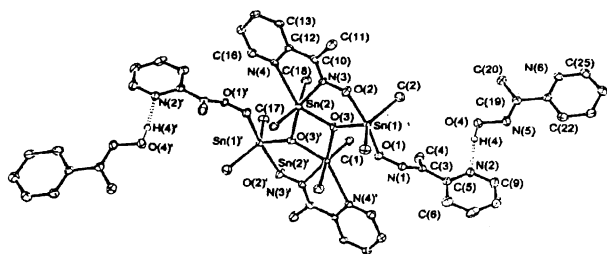
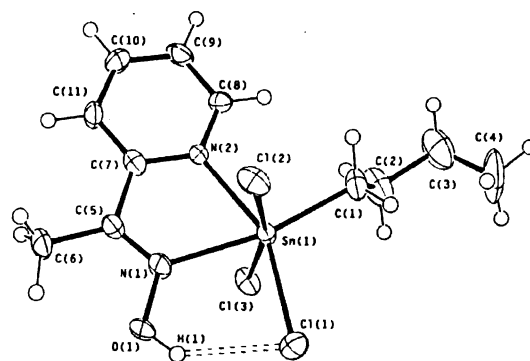


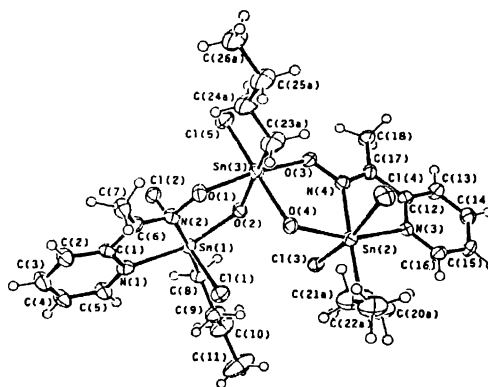
Fig. 13. Crystal structure of $[\{Me_2Sn(ONC(Me)C_5H_4N-2)\}_2O]_2 \cdot 2[2-Py(Me)C=NOH]$.

complex with that in the free acid⁷⁸.

Monoorganotin(IV) trichloride adducts of these functionalised oximes in 1 : 1 and 1 : 2 molar ratios have also been synthesized⁸⁰. The ^{119}Sn NMR spectra of all these derivatives displayed a single resonance in the region δ -400 to -406 ppm, which falls in the range of hexa-coordinated tin atom. Crystal structure analysis of the adduct $BuSnCl_3 \cdot HON=C(Me)Py$ (I) and its hydrolysis product $[BuSnCl_2\{ON=C(Me)Py\}O]_2SnBuCl$ (II) revealed very interesting bonding features⁸¹. In compound (I) both C=N and ring nitrogens are taking part in coordination to give a distorted octahedral environment around tin atom (Fig. 14a). Compound (II) appeared to be a trinuclear species with Sn-O-Sn bonds, again with hexa-coordinated tin atoms (Fig. 14b).



(a)



(b)

Fig. 14. Crystal structures of (a) $BuSnCl_3 \cdot HON=C(Me)Py$ and (b) $[BuSnCl_2\{ON=C(Me)Py\}O]_2SnBuCl$.

It would be worthwhile to mention here, that condensation reaction of R_2SnO with salicylaldoxime afforded a new

class of trinuclear organotin clusters $[R_2Sn]_2(R_2SnO)-(ONZO)(ONZO)(HONZO)]^{82}$. The interesting feature of these trinuclear species is that, the monofunctional μ_2 -bridging ligand [bridging two five-coordinated tin atoms Sn-3 and Sn-2] is susceptible to the attack of a nucleophile. Several reactions have been reported by substituting this μ_2 -bridging ligand and every time the same structure was obtained e.g. ⁸³.

Since oximes are an important class of organic ligands which can form salts and complexes, some volatile triorganotin(IV) complexes have also been synthesized with internally functionalized oximes⁸⁴. On the basis of tin-hydrogen [$^2J(^{119}Sn-^1H)$] and tin-carbon [$^1J(^{119}Sn-^{13}C)$] coupling constants as well as the range of ^{119}Sn chemical shifts, a tetrahedral geometry around the tin atom has been proposed through oxygen atom of the ligand moiety.

Diorganotin(IV) bis chelates have also received much attention⁸⁵⁻⁸⁸. In the X-ray crystal structure of bis(4-benzyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-onato) dibutyl tin(IV), the butyl groups are occupying the *trans* positions of the octahedron. Four oxygen atoms of the pyrazolone moieties and the central tin atom lie in the same plane⁸⁵. Similar kind of structure has been observed for sulphur donor chelates⁸⁶. The molecule, dibutyltinbis(neopentylenedithiophosphate) has a distorted *trans* octahedral geometry (Fig. 15).

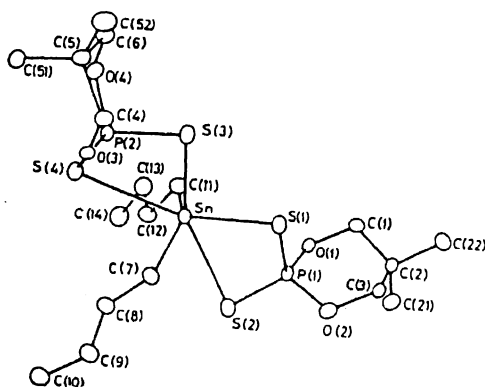


Fig. 15. Crystal structure dibutyltinbis(neopentylenedithiophosphate).

Some metalloorganic derivatives of tin(II)^{87,88} and (IV)⁸⁹⁻⁹⁴ have also been synthesized. Crystal structure analysis of $SnCl_2$ bis(*N,N*-dithiocarbamato-*S,S*) revealed a *cis*-octahedral geometry around the tin atom with Cl-Sn-Cl angle of 91.85(3) (Fig. 16)⁹¹.

The usefulness of lead(II) and (IV) compounds has generated a considerable research activities around them for a long time. Lead zirconium titanate (PZT) is a promising

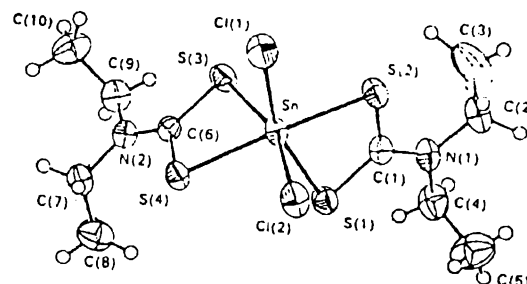


Fig. 16. $SnCl_2$ bis(*N,N*-dithiocarbamato-*S,S*).

material in the field of computers. In continuation of our work on group-14 elements and in order to develop a chelating agent for lead ions, we investigated the interaction of heterocyclic β -diketones with lead(II) isopropoxide⁹⁵. The molecular structure of $Pb[CH_3COC=CON(C_6H_5)]N=CCH_3]_2$ revealed that three molecules are present in the asymmetric unit (Fig. 17). Each lead atom is bonded by two heterocyclic β -diketone ligands. Further each heterocyclic β -diketone is chelated to the central lead atom with two unequal Pb-O bonds. A close inspection of the O-Pb-O bond angles, indicates the stereochemical implications of the lone pair on lead to angular distortions and is occupying an equatorial position of distorted trigonal bipyramidal environment of lead atom.

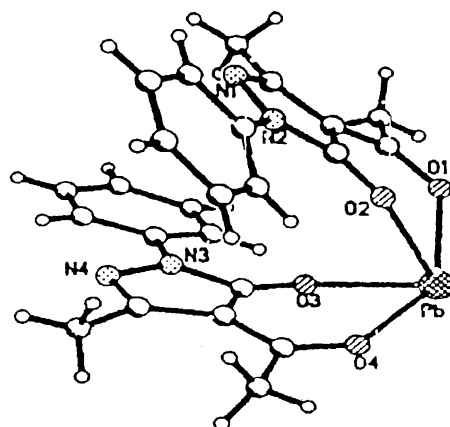


Fig. 17. Crystal structure of $Pb[CH_3COC=CON(C_6H_5)]N=CCH_3]_2$.

Some triethyl lead(IV) complexes have also been synthesized by the metathetical reactions of Et_3PbCl with internally functionalized oximes⁶⁶. These golden yellow viscous oily derivatives have been characterized by their elemental analysis and spectroscopic techniques. The range of ^{207}Pb NMR chemical shift and the value of $^2J(H-Pb)$

and $^nJ(\text{C-Pb})$ [$n = 1$ and 2] indicate tetrahedral coordination at Pb atom.

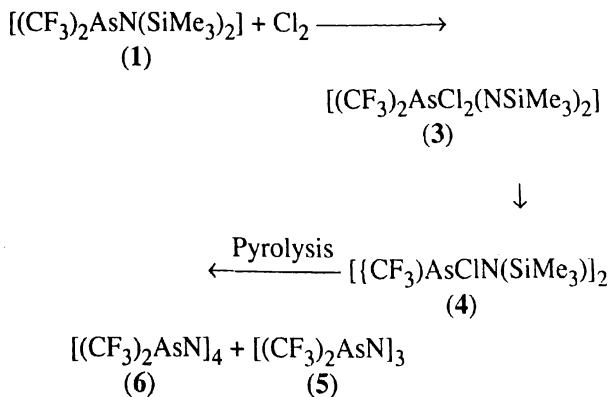
Attempts to distill these *in vacuo* lead to decomposition to give tetraethyl lead (confirmed by ^1H NMR).



Group 15 metalloorganics

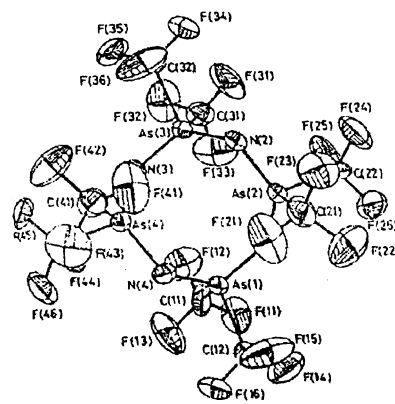
Interest in the chemistry of group 15 elements is growing continuously because of the structural variations, synthetic challenges and wide ranging applications found in the metalloorganic compounds of these elements^{96–98}. These compounds are now extensively used as molecular precursors in MOCVD and sol-gel techniques to deposit a wide variety of inorganic materials including semiconducting materials. Besides these, organometallic compounds of group 15 elements also exhibit biocidal properties and find extensive applications in organic synthesis⁹⁹. Although several metal xanthates, dithiocarbonates and dithiophosphates have been used as molecular precursors in CVD processes for the synthesis of metal-sulphides, but the use of group 15 organometallic derivatives with these ligands for the preparation of pure M_2S_3 is of more recent origin. A considerable amount of research work has been reported from our laboratory on metallo-organic compounds of group 15 elements.

Earlier studies on arsenic derivatives in its both +3 and +5 oxidation states revealed interesting structural features^{100–116}. Formation of two new aminoarsines $[(\text{CF}_3)_2\text{AsN}(\text{SiMe}_3)_2]$ (**1**) and $[(\text{CF}_3)\text{As}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**2**) have been reported¹⁰⁷. Oxidative chlorination of **1** gave an intermediate product $[(\text{CF}_3)_2\text{AsCl}_2(\text{NSiMe}_3)_2]$ ¹¹⁰ (**3**) and $[(\text{CF}_3)\text{AsClN}(\text{SiMe}_3)_2]$ ¹⁰⁸ (**4**). Pyrolysis of (**4**) yielded trimeric (**5**) and tetrameric (**6**) arsazenes.

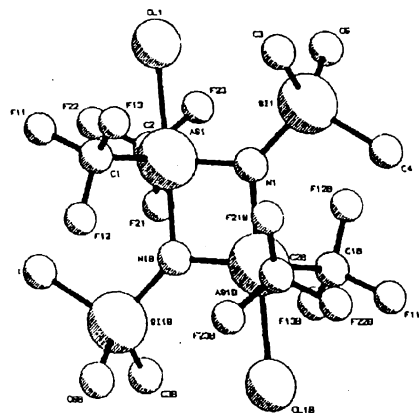


Crystal structure analysis of tetrameric $[(\text{CF}_3)_2\text{AsN}]_4$ (**6**) revealed that there is a barely significant alternation of the As-N bond length in the eight-membered ring (Fig. 18a). Similarly it had been shown that $[(\text{CF}_3)\text{AsClN}(\text{SiMe}_3)_2]$

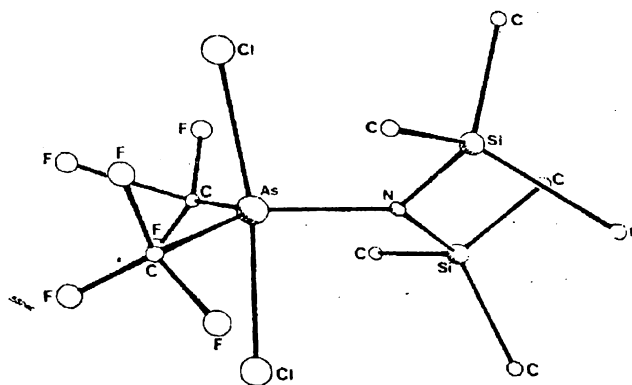
(**4**)¹⁰⁸ (Fig. 18b) was the first organoarsenone in which four-membered As_2N_2 ring contained five-coordinated As atoms. $[(\text{CF}_3)_2\text{AsCl}_2(\text{NSiMe}_3)_2]$ (**3**)¹¹⁰ exhibits a trigonal bipyramidal geometry with axial chlorine atoms (Fig. 18c).



(a)

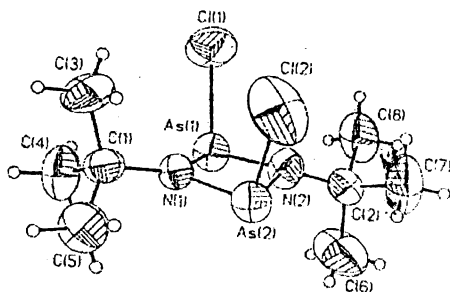


(b)



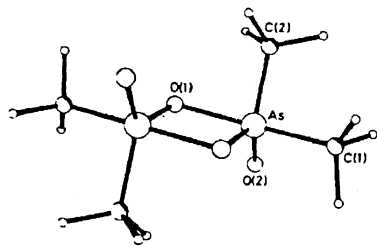
(c)

Fig. 18. Crystal structures of (a) $[(\text{CF}_3)_2\text{AsN}]_4$, (b) $[(\text{CF}_3)\text{AsClN}(\text{SiMe}_3)_2]$ and (c) $[(\text{CF}_3)_2\text{AsCl}_2(\text{NSiMe}_3)_2]$.

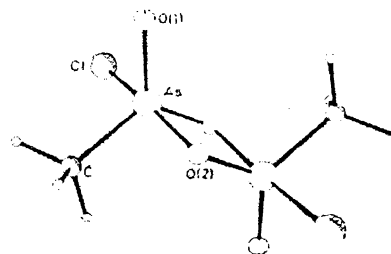

 Fig. 19. Crystal structure of $[t\text{-BuNaAsCl}]_2$.

NMR studies of $[t\text{-BuNaAsCl}]_2$, prepared by a new route¹¹¹ indicated the presence of only one isomer. The four-membered ring As_2N_2 is planar, with coplanar orientation of C-atoms of the *t*-Bu group, as demonstrated by its X-ray diffraction studies (Fig. 19). The two Cl atoms lie 2.073(3) Å to the same side of this plane, which is in contrast to the corresponding methyl analogue (the two Cl atoms are oriented in the opposite direction to each other).

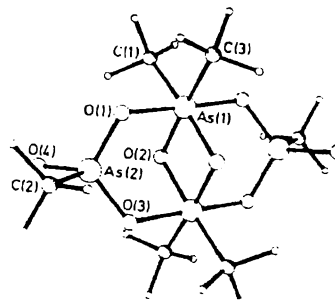
Interesting structural variations in arsoranes promoted us to examine the As-O heterocycles containing trifluoromethyl groups¹¹². Crystal structures of $[\text{As}(\text{CF}_3)_2\text{O}(\text{OH})]_2$ (1), $[\text{As}(\text{CF}_3)\text{O}(\text{OH})\text{Cl}]_2$ (2) and of a novel cage molecule $[\text{As}_4(\text{CF}_3)_6\text{O}_6(\text{OH})_6]$ (3) have been carried out (Fig. 20a-c). The structures of the compounds (1) (Fig. 20a) and (2) (Fig. 20b) are very similar. The arsenic atom is trigonal bipyramidally coordinated with equatorial trifluoromethyl and hydroxyl groups. The four-membered As_2O_2 rings are planar and asymmetrical. In case of compound (3) (Fig. 20c) the four-membered As_2O_2 ring is symmetrical where as the As(1)-O-As(2) bridges are very unsymmetrical. This unsymmetry equalizes the effective coordination states of As atoms, which are normally +3 (with a net charge of +1) and +5 (with a net charge of -1), respectively. The structures reported here indicate that when electron withdrawing groups are attached to an As atom which is also bonded to oxygen, oligomers containing four-membered As_2O_2 rings are formed in preference to monomers having As=O double bonds.



(a)



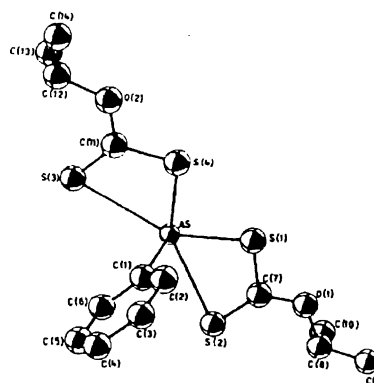
(b)



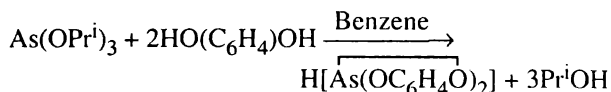
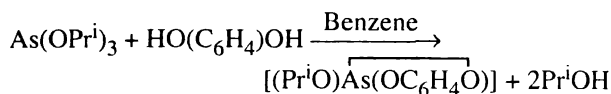
(c)

 Fig. 20. Crystal structures of (a) $[\text{As}(\text{CF}_3)_2\text{O}(\text{OH})]_2$, (b) $[\text{As}(\text{CF}_3)\text{O}(\text{OH})\text{Cl}]_2$ and (c) $[\text{As}_4(\text{CF}_3)_6\text{O}_6(\text{OH})_6]$.

Crystal structure analysis of phenyl bis(*O*-isopropylxanthato-*S,S'*)arsenic(III) revealed square pyramidal geometry around the arsenic atom¹¹⁷. The apical position is occupied by a phenyl group and the stereochemically active lone pair of electrons is present *trans* to it (Fig. 21).


 Fig. 21. Crystal structure of phenyl bis(*O*-isopropylxanthato-*S,S'*)-arsenic(III).

Interaction between arsenic(III)isopropoxide with 1,2-dihydroxybenzene in 1 : 1 and 1 : 2 molar ratios in refluxing benzene under anhydrous conditions, yielded $[(\text{Pr}^i\text{O})\text{As}(\text{OC}_6\text{H}_4\text{O})]$ and $\text{H}[\text{As}(\text{OC}_6\text{H}_4\text{O})]$ ¹¹⁸ :



Further reaction of $\text{H[As(OC}_6\text{H}_4\text{O)}_2]$ with MOCH_3 and pyrrolidine (where $\text{M} = \text{Li, Na and K}$) in 1 : 1 molar ratio yielded products of the type $\text{M[As(OC}_6\text{H}_4\text{O)}_2]$ and $[\text{C}_4\text{H}_8\text{NH}_2][\text{As(OC}_6\text{H}_4\text{O)}_2]$, respectively. It is interesting to mention here that the reaction of $\text{H[As(OC}_6\text{H}_4\text{O)}_2]$ with pyrrolidine in methanol appears to yield initially $[\text{C}_4\text{H}_8\text{NH}_2][\text{As(OC}_6\text{H}_4\text{O)}_2]$. Attempts to crystallize it from methanol yielded a yellow crystalline oxidized solid, $[\text{C}_4\text{H}_8\text{NH}_2][(\text{MeO})_2\text{As(OC}_6\text{H}_4\text{O)}_2]$. X-Ray diffraction study revealed that both 1,2-dihydroxybenzene moieties are asymmetrically chelated to arsenic with two short 1.841 Å and two long 1.868 Å (Fig. 22) As-O bond lengths. Two methoxy groups also bonded to arsenic(V) atom at an average distance of 1.784 Å forming six-coordination around it.

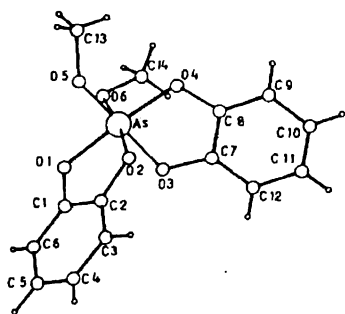
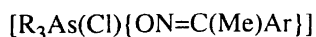
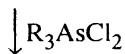
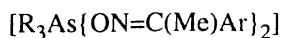
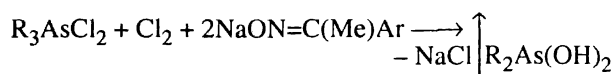
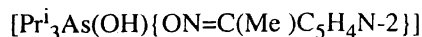
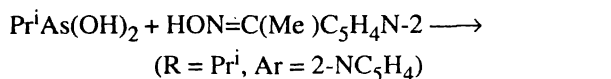


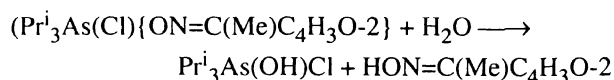
Fig. 22. Crystal structure of $[\text{C}_4\text{H}_8\text{NH}_2](\text{MeO})_2\text{As(OC}_6\text{H}_4\text{O)}_2$.

Recently we reported the synthesis and structure of some triorganoarsenic(V)bis(2-heteroaryl methylketoximate) complexes by the reactions of the type as shown below¹¹⁹:



(where $\text{R} = \text{Pr}^i, \text{Bu}^i$; $\text{Ar} = \text{C}_5\text{H}_4\text{N-2, C}_4\text{H}_3\text{O-2, C}_4\text{H}_3\text{S-2}$)

On the basis of NMR (^1H and ^{13}C) data, it was concluded that both the hetero atoms (oxime-N and heteroatom present on the aromatic ring) are not taking part in coordination with central As atom. Controlled hydrolysis of a representative monochloro-complex $[\text{Pr}^i_3\text{As(Cl)\{ON}=\text{C(Me)C}_4\text{H}_3\text{O-2}\}}]$ has been carried out to yield crystals of $\text{Pr}^i_3\text{As(OH)Cl}$ which was confirmed by single crystal X-ray diffraction study.



In the structure of $[\text{Pr}^i_3\text{As(OH)}]^+\text{Cl}^-$, the $[\text{Pr}^i_3\text{As(OH)}]^+$ core is exhibiting a distorted tetrahedral geometry around As^V atom (Fig. 23).

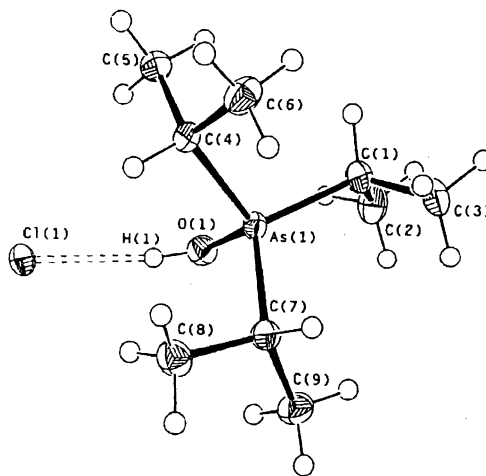


Fig. 23. Crystal structure of $[\text{Pr}^i_3\text{As(OH)}]^+\text{Cl}^-$.

The Cl^- ion is bonded with the OH group of the $\text{Pr}^i_3\text{As(OH)}^+$ unit, through hydrogen bonding $[\text{H(1)-Cl(1)} 2.177 \text{ Å}]$.

Similar kind of complexes of antimony(V) have also been reported with simple¹²⁰ as well as more recently with internally functionalized oximes^{121,122} by a similar route as indicated above for corresponding arsenic derivatives. Crystal structure analysis of $[\text{Me}_3\text{Sb\{ON}=\text{C(Me)C}_4\text{H}_3\text{O-2}\}_2]$, $[\text{Me}_3\text{Sb\{ON}=\text{C(Me)C}_4\text{H}_3\text{S-2}\}_2]$ and $[\text{Ph}_3\text{Sb\{ON}=\text{C(Me)C}_5\text{H}_4\text{N-2}\}_2]$ exhibit trigonal bipyramidal monomeric structures with no intermolecular interactions. Two oxime moieties are coordinated to the central antimony atom with the two oxygen atoms occupying axial position (Fig. 24).

Some complexes of antimony in its oxidation number three have also been prepared¹²³⁻¹²⁸. X-Ray crystallo-

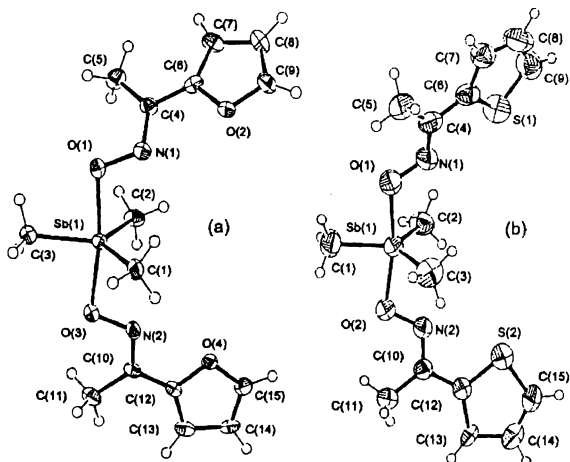


Fig. 24. Crystal structures of (a) [Me₃Sb{ONC(Me)C₄H₃O-2}₂]. (b) [Me₃Sb{ONC(Me)C₄H₃S-2}₂].

graphic investigations on H[Sb(SCH₂CH₂O)₂] have provided the existence of weak intermolecular 'secondary bonding' (the chelate ring remains unsymmetrical) and the overall coordination polyhedron is a distorted trigonal bipyramid (Fig. 25)¹²³. The corresponding *O, O'*-analogue NH₄[Sb(O-C₆H₄-O)₂] exhibits two five-membered chelate ring of 1,2-dihydroxy benzene in its structure¹²⁵. Other bimetallic heterocycles M[Sb{OC(Me)₂C(Me)₂O}₂] (M = Li, Na, K and also NiCl and Ni) containing five-membered chelate rings, have been synthesized by the reaction of Sb(OPrⁱ)₃ with appropriate ligands¹²⁶.

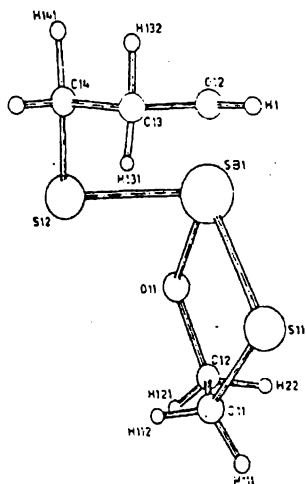
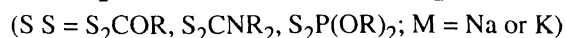
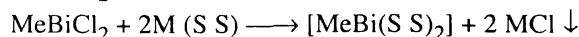
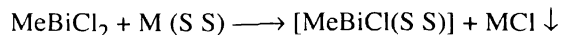


Fig. 25. Crystal structure of H[Sb(SCH₂CH₂O)₂].

Group V chalcogenide materials, including binary and ternary compounds such as Bi₂Te₃ and CuSb₂, have at-

tracted considerable attention due to their good photovoltaic properties and high thermoelectric power^{129,130}. In this context some monoorganobismuth(III) complexes of xanthates, dithiocarbonates and dialkyldithiophosphates in 1 : 1 and 1 : 2 stoichiometry have been prepared and characterized^{131,132}.



These compounds have been characterized by their elemental analysis and spectroscopic (IR, ¹H, ¹³C, ³¹P and ¹³C CPMAS NMR) data. Crystal structure analysis of [MeBiCl{S₂CNEt₂}] has also been carried out¹³². The central Bi atom is penta-coordinated with Bi-Cl-Bi bridges resulting in a polymeric structure (Fig. 26). The dithiocar-

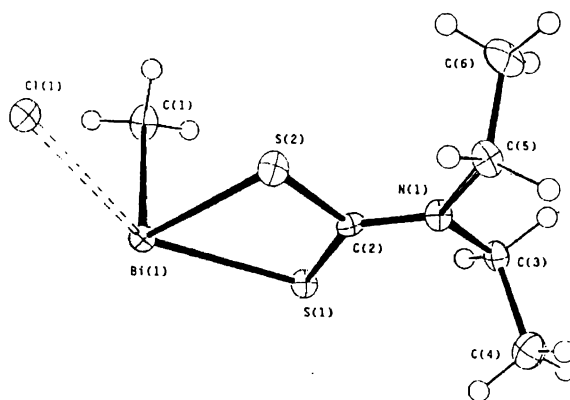


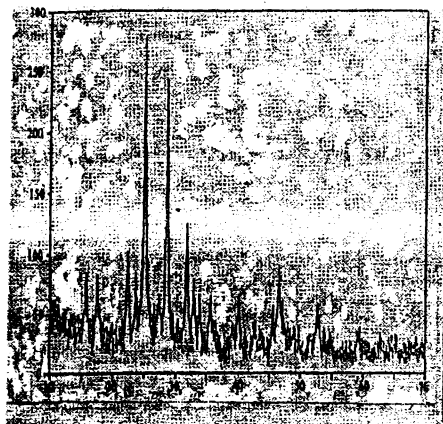
Fig. 26. Crystal structure of [MeBiCl(S₂CNEt₂)].

bamate moiety is chelated in an unsymmetrical manner [Bi(1)-S(1); 2.6702(19) Å and Bi(1)-S(2); 2.6786(19) Å] :

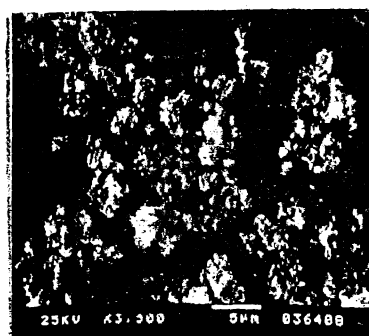
Presence of two sets of resonances for the ligand carbon atoms in the ¹³C CPMAS NMR spectra of 1 : 2 derivatives, indicated the dimeric structures of these compounds in the solid state¹³¹. X-Ray diffraction analysis of [MeBi(S₂COMe)₂] revealed a distorted square pyramidal environment around bismuth atom. The two bidentate xanthate ligands lie in the plane each having one shorter [Bi(1)-S(1); ~2.747 Å] and one longer bond [Bi(1)-S(2); 2.918 Å]. A longest bond distance of 3.253(1) Å is present between central Bi atom and S atom of the adjacent molecule to give a polymeric structure.

To assess whether these complexes can serve as molecular precursors for the synthesis of the pure Bi₂S₃ either by spray or aerosol assisted CVD methods, thermal behaviour of few representative complexes have been studied. When

[MeBi{S₂C(OPrⁱ)₂}], was refluxed in xylene a blackish grey powder was obtained. It has been identified as Bi₂S₃ from XRD pattern (Fig. 27a). The scanning electron micrographs (Fig. 27b) of this product taken at different resolutions showed large aggregates of microcrystals.



(a)



(b)

Fig. 27. (a) XRD pattern and (b) scanning electron micrographs of Bi₂S₃.

The above results suggest that the earlier reported thio-complexes of bismuth(III) in which BiS₆ core is present, may also be the potential precursors for pure Bi₂S₃¹³³.

Acknowledgement

I am grateful to Drs. Vinita Sharma, Shama Chauhan and Mr. Amit K. Jain for their very kind help in the preparation of the manuscript and thankful to D.S.T. and U.G.C., New Delhi for financial support.

References

1. S. S. Kistler, *Nature*, 1931, 127, 741.
2. G. A. Nicolason and S. J. Teichner, *Bull. Soc. Chim. Fr.*, 1968, 5,

1906; J. D. Mackenzie and D. R. Ulrich (eds.), "Ultrastructure Processing of Advanced Ceramics", Wiley, New York, 1988; M. A. Aegerter, M. Jafellicci, J. D. F. Souza and E. D. Zanotto (eds.), "Sol-gel Science and Technology", Word Scientific, New York, 1988; C. J. Binker and G. N. Scherer, "Sol-gel Science, The Physics and Chemistry of Sol-gel Processing", Academic Press, New York, 1990.

3. Y. A. Attia (ed.), "Sol-gel Processing and Applications", Plenum Press, New York, 1994; F. D. Gnanam (ed.), "Sol-gel Processing of Advanced Ceramics", Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi, 1996; D. C. Bradely, R. C. Mehrotra, I. P. Rothwell and A. Singh, "Alkoxo and Aryloxo Derivatives of Metals", Academic Press, London, 2001; N. Y. Turova, E. P. Turevskaya, V. G. Kessler and M. I. Yanovskaya, "The Chemistry of Metal Alkoxides", Kluwer Academic Publishers, London, 2002.
4. R. Bohra (ed.), "Advances in Metallo-Organic Chemistry", RBSA Publishers, Jaipur, India, 1999; R. Bohra, A. Singh and R. C. Mehrotra (eds.), "The Chemistry and Applications of Alkoxy, Aryloxy and Allied Derivatives of Elements", RBSA Publishers, Jaipur, 2003.
5. R. C. Mehrotra, A. K. Rai, A. Singh and R. Bohra, *Inorg. Chim. Acta*, 1975, 103, 91.
6. (a) R. C. Mehrotra, A. K. Rai, P. N. Kapoor and R. Bohra, *Inorg. Chim. Acta*, 1976, 16, 237; (b) R. C. Mehrotra, R. Bohra and D. P. Gaur, "Metal β-Diketonates and Allied Derivatives", Academic Press, London, 1978, 382.
7. E. N. Vasanta, R. Bohra and R. C. Mehrotra, *Proc. Indian Nat. Sci. Acad.*, 1981, 47A, 511.
8. V. K. Jain, R. Bohra and R. C. Mehrotra, *Structure and Bonding*, 1982, 52, 147.
9. R. C. Mehrotra and R. Bohra, "Metal-Carboxylates", Academic Press, London, 1983, 396.
10. R. Bohra and H. W. Roesky, *Adv. Inorg. Radiochem.*, 1984, 28, 203.
11. R. Bohra, R. K. Mehrotra and R. C. Mehrotra, *Rasayan Samiksha*, 1986, 2, 1.
12. R. Bohra and A. Gupta, *J. Indian Chem. Soc.*, 2003, 80, 281.
13. V. Sharma and R. Bohra, "Advances in Organometallics", Nova Science Publications, New York, 2005 (in press).
14. L. G. Hubert-Pfalzgraf, *New J. Chem.*, 1987, 11, 663.
15. T. J. Boyle and H. N. Al-Shareef, *J. Mater. Sci.*, 1997, 32, 2263.
16. C. Sanchez, B. Lebeau, F. Ribot and M. In, *J. Sol-Gel Sci. Tech.*, 2000, 19, 31.
17. A. H. Cowley and R. A. Jones, *Angew. Chem. Int. Ed. Engl.*, 1989, 28, 1208.
18. D. A. Atwood, R. A. Jones and A. H. Cowley, *J. Organomet. Chem.*, 1992, 434, 143.
19. J. L. Shay and J. H. Wernick, "Ternary Chalcopyrite Semiconductor. Growth, Electronic Properties and Applications", Pergamon Press, Elmsford, New York, 1975.

20. D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.
21. R. C. Mehrotra and A. Singh, "Sol-gel Processing of Advanced Ceramics", Gnanam (ed.), 1996, 11.
22. S. N. Vaidya, *Bull. Mater. Sci.*, 1999, **22**, 287.
23. K. Tadanaga, J. Morinaga and T. Minami, *J. Sol-Gel. Sci. Tech.*, 2000, **19**, 211.
24. R. C. Mehrotra, *J. Indian Chem. Soc.*, 1953, **30**, 585.
25. J. W. Akitt and R. H. Duncan, *J. Magn. Reson.*, 1974, **15**, 162.
26. R. C. Mehrotra and A. K. Rai, *Polyhedron*, 1991, **10**, 1967.
27. K. Folting, W. E. Streib, K. G. Caulton, O. Poncelet and L. G. Hubert-Pfalzgraf, *Polyhedron*, 1991, **10**, 1639.
28. D. J. Brauer and G. D. Stucky, *J. Am. Chem. Soc.*, 1969, 5462.
29. J. H. Wengrovius, M. F. Garbaskas, E. A. Williams, R. C. Going, P. E. Donahue and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 982.
30. P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, 1973, **3**, 67.
31. A. Dhammani, R. Bohra and R. C. Mehrotra, *Polyhedron*, 1998, **17**, 103.
32. N. Sharma, R. K. Sharma and R. Bohra, *Main Group Met. Chem.*, 2002, **24**, 781.
33. S. Nagar, A. Dhammani, R. Bohra and R. C. Mehrotra, *J. Coord. Chem.*, 2002, **55**, 381.
34. S. Nagar, R. Bohra and R. C. Mehrotra, *Indian J. Chem., Sect. A*, 2002, **41**, 2288.
35. S. Nagar, R. Bohra and R. C. Mehrotra, *Synth. React. Inorg.-Org. Met. Chem.*, 2002, **32**, 1825.
36. A. K. Jain, R. Bohra, R. C. Mehrotra, S. Nagar and S. Sharma, *Heteratom Chem.*, 2003, **14**, 518.
37. N. Sharma, R. K. Sharma and R. Bohra, unpublished results.
38. A. Dhammani, R. Bohra and R. C. Mehrotra, *Polyhedron*, 1996, **15**, 733.
39. (a) A. Dhammani, R. Bohra and R. C. Mehrotra, *Polyhedron*, 1995, **14**, 733; (b) R. Bohra, A. Dhammani, R. K. Sharma and R. C. Mehrotra, *Synth. React., Inorg. Metal-Org. Chem.*, 2001, **31**, 681.
40. S. Nagar, R. Bohra and R. C. Mehrotra, *Main Group Met. Chem.*, 2002, **25**, 277.
41. A. Vyas and R. Bohra, *Synth. React. Inorg.-Org. Met. Chem.*, 1996, **26**, 1691.
42. A. Vyas, N. Sharma, R. K. Sharma and R. Bohra, *Main Group Met. Chem.*, 2001, **24**, 373.
43. N. Sharma, R. K. Sharma, R. Bohra, J. E. Drake, M. B. Hursthouse and M. E. Light, *J. Chem. Soc., Dalton Trans.*, 2002, 1631.
44. N. Sharma, R. K. Sharma and R. Bohra, *J. Chem. Res.*, 2002, 622.
45. N. Sharma, A. K. Jain, R. K. Sharma, R. Bohra, T. E. Drake, M. B. Hursthouse and M. E. Light, *Polyhedron*, 2003, **22**, 2943.
46. (a) A. K. Jain, A. Gupta, R. Bohra and R. C. Mehrotra, *Main Group Met. Chem.*, 2003, **26**, 111; (b) A. K. Jain, R. Bohra and R. C. Mehrotra, *Main Group Met. Chem.*, 2004, **27**, 113.
47. A. K. Jain, A. Gupta, R. Bohra, R. C. Mehrotra, I.-P. Lorentz and H. Piotrowski, unpublished results.
48. R. Apodaka and W. Xiao, *Org. Lett.*, 2001, **3**, 1745.
49. M. Cera, E. Cerrada, M. Laguna, J. A. Mata and H. Teruel, *Organometallics*, 2002, **21**, 121.
50. A. Ricci, F. Anglucchi, M. Bassetti and C. L. Sterzo, *J. Am. Chem. Soc.*, 2002, **124**, 1060.
51. M. A. Girasolo, T. Pizzino, C. Mansueto, G. Valle and G. C. Stocco, *Appl. Organomet. Chem.*, 2000, **14**, 197.
52. K. Rubina, E. Abele, P. Arsenyan, R. Abele, M. Veveris and E. Lukevics, *Met.-Based Drugs*, 2001, **8**, 85.
53. B. Kozyrkin, J. de physique IV: Proceedings 2001, 11 (Pr3. thirteenth European Conference on chemical vapour Deposition 2001), Pr 3/617 Pr 3/619 (*Chem. Abstr.*, 2002, **136**, 29799).
54. F. S. Hintermaier and T. H. Baum, U.S. US 6, 214, 105 (CI 106-287. 19 ; C09 K3/00) 10 Apr. 2001, US Appl. 95, 372, 20 Nov. 1997 (*Chem. Abstr.*, 2001, **134**, 28816).
55. M. Verdenelli, S. Parola, L. G. Hubert-Pfalzgraf and S. Lecocq, *Polyhedron*, 2000, **19**, 2069.
56. B. Jousseau, H. Riague, T. Toupance, M. Lahcini, P. Mountiford and B. R. Tyrrell, *Organometallics*, 2002, **21**, 4590.
57. R. G. Gordon, *MRS Bulletin*, 2000, **25**, 52.
58. D. C. Bradley, L. Kay and W. Wardlaw, *Chem. and Ind.*, 1953, 746.
59. D. C. Bradley, L. Kay and W. Wardlaw, *J. Chem. Soc.*, 1956, 4916.
60. D. C. Bradley, L. Kay and W. Wardlaw, *J. Chem. Soc.*, 1958, 3656.
61. R. C. Mehrotra and G. Chandra, *J. Indian Chem. Soc.*, 1962, **39**, 235.
62. R. C. Mehrotra and G. Chandra, *J. Chem. Soc.*, 1963, **520**, 2804.
63. R. C. Mehrotra and G. Chandra, *Indian J. Chem.*, 1965, **3**, 497.
64. M. Pathak, R. Bohra and R. C. Mehrotra, *J. Chem. Res.*, 2004, 377.
65. M. Pathak, R. Bohra and R. C. Mehrotra, *J. Chem. Res.*, 2003, 567.
66. V. Sharma, S. Agarwal, R. Bohra and V. K. Jain, *J. Chem. Res.*, 2004, 273.
67. M. Pathak, R. Bohra, R. C. Mehrotra, I.-P. Lorentz and H. Piotrowski, *Trans. Met. Chem.*, 2003, **28**, 187.
68. V. Sharma, V. Sharma, R. Bohra, R. Ratnani, V. K. Jain, J. E. Drake, M. B. Hursthouse and M. E. Light, 2004, unpub-

- lished results.
69. (a) M. Pathak, R. Bohra, R. C. Mehrotra, I.-P. Lorentz and H. Piotrowski, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2493; (b) V. Sharma, V. Sharma, R. Bohra, R. Ratnani, V. K. Jain, J. E. Drake, M. B. Hursthouse and M. E. Light, 2004, unpublished results.
70. S. Sogani, A. Singh, R. Bohra, R. C. Mehrotra and M. Noltemeyer, *J. Chem. Soc., Chem. Commun.*, 1991, 738.
71. K. Sakamoto, H. Ikeda, H. Akashi, T. Fukuyama, A. Orita and J. Otera, *Organometallics*, 2000, **19**, 3242 and references therein.
72. V. Sharma, R. K. Sharma and R. Bohra, in "Chemistry of Alkoxy Derivatives of Elements", eds. R. Bohra, A. Singh and R. C. Mehrotra, RBSA Publishers, Jaipur, 2003.
73. F. Ribot, F. Banse, C. Sanchez, M. Lahcini and B. Jousseume, *J. Sol-Gel Sci. Technol.*, 1997, **8**, 529.
74. S. Boutet, A. Gamard, B. Jousseume, T. Toupance, G. Campet and H. Cachet, *Main Group Met. Chem.*, 2002, **25**, 59.
75. (a) B. K. Agrawal, Y. P. Singh, R. Bohra, G. Srivastava and A. K. Rai, *J. Organomet. Chem.*, 1993, **444**, 47; (b) K. Hübner, H. W. Roesky, M. Noltemeyer and R. Bohra, *Chem. Ber.*, 1991, **124**, 515.
76. J. Beckmann, K. Jurkschat, S. Rabe, M. Schürmann and D. Dekternieks, *Z. Anorg. Chem.*, 2001, **627**, 458.
77. V. Dokorou, M. A. Demertzis, J. P. Jasinski and D. Kovalá-Demertzi, *J. Organomet. Chem.*, 2004, **689**, 317.
78. V. Sharma, R. Bohra, R. Ratnani, V. K. Jain, J. E. Drake, M. B. Hursthouse and M. E. Light, *J. Organomet. Chem.*, 2002, **651**, 98.
79. V. Sharma, R. Bohra, R. Ratnani, V. K. Jain, J. E. Drake, M. E. Light and M. B. Hursthouse, *J. Organomet. Chem.*, 2002, **664**, 66.
80. V. Sharma, Ph.D. Thesis, University of Rajasthan, Jaipur, India, 2003.
81. V. Sharma, R. Bohra, R. Ratnani, V. K. Jain, J. E. Drake, M. E. Light and M. B. Hursthouse, unpublished results.
82. F. Kayser, M. Biesemans, M. Boualam, E. R. T. Tiekink, A. El-Khloufi, J. Meunier, O. Piret, A. Bouhdid, K. Jurkschat, M. Gielen and R. Willem, *Organometallics*, 1994, **13**, 1098.
83. F. A. G. Mercier, A. Meddour, M. Gielen, M. Bieseaus, R. Willems and E. R. T. Tiekink, *Organometallics*, 1998, **17**, 5933.
84. V. Sharma, R. K. Sharma, R. Bohra and V. K. Jain, *Main Group Met. Chem.*, 2002, **25**, 445.
85. S. Saxena, R. Bohra and A. K. Rai, *Inorg. Chim. Acta*, 1990, **173**, 191.
86. A. A. S. El-Khaldy, Y. P. Singh, R. Bohra, R. K. Mehrotra and G. Srivastava, *Main Group Met. Chem.*, 1991, **14**, 305.
87. A. Jain, S. Saxena, R. Bohra and A. K. Rai, *Main Group Met. Chem.*, 1995, **18**, 139.
88. J. Sharma, Y. P. Singh, R. Bohra and A. K. Rai, *Polyhedron*, 1996, **15**, 1097.
89. S. Sharma, R. Bohra and R. C. Mehrotra, *Indian J. Chem., Sect. A*, 1990, **29**, 911.
90. S. Sharma, R. Bohra and R. C. Mehrotra, *Synth. React. Inorg. Metal-Org. Chem.*, 1991, **21**, 741.
91. R. Bohra, S. Sharma and A. Dhammani, *Acta Cryst. (C)*, 1994, **50**, 1447.
92. R. Bohra, S. Sharma and A. Dhammani, unpublished results.
93. A. Jain, S. Saxena, R. Bohra and A. K. Rai, *Main Group Met. Chem.*, 1995, **18**, 661.
94. S. Sharma, R. Bohra and R. C. Mehrotra, *Polyhedron*, 1996, **15**, 1525.
95. A. Jain, S. Saxena, A. K. Rai, R. Bohra and H. Q. Wang, *Main Group Met. Chem.*, 2003, **26**, 1.
96. C. Jones, *Coord. Chem. Rev.*, 2001, **215**, 151.
97. I. Mohammadpoor-Baltork, A. R. Knosropour and H. Aliyan, *Syn. Commun.*, 2001, **31**, 3411.
98. A. Gupta, R. K. Sharma and R. Bohra, "Chemistry of Alkoxy Derivatives of Elements", eds. R. Bohra, A. Singh and R. C. Mehrotra, RBSA Publishers, Jaipur, India, 2003.
99. I. Mohammadpoor-Baltork, R. Ahmad and H. Alufan, *J. Chem. Res. Synopsis*, 2001, **7**, 280.
100. R. C. Mehrotra, A. K. Rai and R. Bohra, *J. Indian Chem. Soc.*, 1973, **51**, 304.
101. R. C. Mehrotra, A. K. Rai and R. Bohra, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 167.
102. R. C. Mehrotra, A. K. Rai and R. Bohra, *Synth. React. Inorg. Metal-Org. Chem.*, 1975, **5**, 289.
103. V. K. Jain, R. Bohra and R. C. Mehrotra, *Synth. React. Inorg. Metal-Org. Chem.*, 1979, **2**, 491.
104. V. K. Jain, R. Bohra and R. C. Mehrotra, *J. Organomet. Chem.*, 1980, **33**, 2749.
105. V. K. Jain, R. Bohra and R. C. Mehrotra, *Inorg. Chem. Acta*, 1980, **44**, 265.
106. V. K. Jain, R. Bohra and R. C. Mehrotra, *Inorg. Chem. Acta*, 1981, **51**, 191.
107. R. Bohra, H. W. Roesky, J. Lucas, M. Noltemeyer and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1011.
108. R. Bohra, H. W. Roesky and W. S. Sheldrick, *J. Fluorine Chem.*, 1983, **22**, 199.
109. V. K. Jain, R. Bohra and R. C. Mehrotra, *Indian J. Chem., Sect. A*, 1983, **22**, 445.
110. R. Bohra and H. W. Roesky, *J. Fluorine Chem.*, 1984, **25**, 145.
111. R. Bohra, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *Acta Crystallogr.*, 1984, **C40**, 1150.
112. R. Bohra, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 2011.
113. T. Athar, R. Bohra and R. C. Mehrotra, *Main Group Met.*

- Chem.*, 1987, **10**, 399.
114. T. Athar, R. Bohra and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1989, **66**, 189.
 115. T. Athar, R. Bohra and R. C. Mehrotra, *Indian J. Chem., Sect. A*, 1989, **28**, 302.
 116. T. Athar, R. Bohra and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1990, **67**, 535.
 117. R. Karra, Y. P. Singh, R. Bohra and A. K. Rai, *J. Cryst. Spect. Res.*, 1992, **22**, 721.
 118. Sanjeev Bhargava, Ph.D. Thesis, University of Rajasthan, Jaipur, India, 1992.
 119. A. Gupta, R. K. Sharma and R. Bohra, *J. Organomet. Chem.*, 2003, **667**, 61.
 120. V. K. Jain, R. Bohra and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1980, **57**, 408.
 121. A. Gupta, R. K. Sharma, R. Bohra, V. K. Jain, J. E. Drake, M. B. Hursthouse and M. E. Light, *J. Organomet. Chem.*, 2002, **645**, 118.
 122. A. Gupta, R. K. Sharma, R. Bohra, V. K. Jain, J. E. Drake, M. B. Hursthouse and M. E. Light, *Polyhedron*, 2002, **21**, 2387.
 123. A. K. Sen Gupta, R. Bohra and R. C. Mehrotra, *Inorg. Chim. Acta*, 1990, **170**, 191.
 124. S. Sharma, R. Bohra and R. C. Mehrotra, *J. Indian Chem. Soc.*, 1990, **67**, 945.
 125. A. K. Sen Gupta, R. Bohra, R. C. Mehrotra and K. Das, *Main Group Met. Chem.*, 1990, **13**, 321.
 126. A. K. Sen Gupta, R. Bohra and R. C. Mehrotra, *Synth. React. Inorg. Metal-Org. Chem.*, 1991, **21**, 445.
 127. A. K. Sen Gupta, R. Bohra and R. C. Mehrotra, *Indian J. Chem., Sect. A*, 1991, **30**, 588.
 128. S. Sharma, R. Bohra and R. C. Mehrotra, *Indian J. Chem., Sect. A*, 1993, **32**, 59.
 129. P. Lostak, A. Drosar, A. Krejcova, L. Benes, J. S. Dyek, W. Chem and C. Uher, *J. Cryst. Growth*, 2001, **222**, 565.
 130. O. Salminen, A. Ozoles, P. Riihola and P. Moenkkonn, *J. Appl. Phys.*, 1993, **78**, 718.
 131. A. Gupta, R. K. Sharma, R. Bohra, V. K. Jain, J. E. Drake, M. B. Hursthouse and M. E. Light, *J. Organomet. Chem.*, 2003, **678**, 122.
 132. A. K. Jain, R. Bohra, J. E. Drake, M. B. Hursthouse and M. E. Light, 2004, unpublished results.
 133. R. Bohra, H. P. S. Chauhan, G. Srivastava and R. C. Mehrotra, *Phosphorus, Sulphur and Silicon*, 1991, **60**, 167.