

Studies on Complex of Sn (iv, ii), Bi (iii) and Sd (iii) with substituted in Cyclohexthio-Pyrrolides

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Abstract

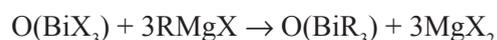
Bismuth is a Vth A group element of periodic table having a electronic configuration [Xe] 4f¹⁴5d¹⁰6s²6p³. Since Bismuth is a less common element, so very few of its complexes are known till now. From electronic configuration, the possible oxidation states shown by Bismuth are +3 and +5. The electronic structure of next inert gas could be obtained by the gain of three electrons, where Bismuth has valency three and Compound has covalent nature. Here a considerable energies are involved, so, -3 oxidation state will be unstable. Moreover loss of valence electrons is similarly difficult to achieve, because of the high Ionization potential. The +5 oxidation state ion certainly does not exist. Therefore, +3 oxidation state is most stable form.

Keywords: Structure, Compound, Element, Oxidation, Halogen, Crystal Dilute, Metallic

Bismuth does not occur in allotropic form like other element of the group. Bismuth is bright in normal form and its appearance in metallic form has crystal structure similar to that of black phosphorous; on heating it burns to form oxides. It reacts directly and readily with halogen and some of other non-metals. Bismuth forms alloys with various other metals. Dilute non-oxidising acids does effect on Bismuth. While, it dissolves in nitric acid and forms nitrate. Bismuth forms trihalides of the formula BiX₃ with halogen. Moreover, trichlorides and trifluorides of Bismuth, takes additional halide ion to form complex halo anions such as [BiCl₅]²⁻ and [BiF₅]²⁻ and the structures of this complex halo anions are irregular polyhedera, because there are ushared electron pairs present in valence shells of metal.

If Bismuth salt solution is treated with hydrogen sulphide, a dark brown precipitate of Bi₂S₃ separated

out. It is not acidic and is insoluble in alkali-sulphides. Selenides and tellurides of Bismuth can be obtained, which are semi-conductor in nature organobismuth compounds, which are very few in number, are not very stable. The organoderivatives may be prepared by various ways, but the simplest way is, by the treatment of halides or oxyhalides with Grignard reagents. e.g.



the compound R₃BiO can be obtained by above method is quite stable form.

The aqueous solution of hydrated Bismuth (III) ion

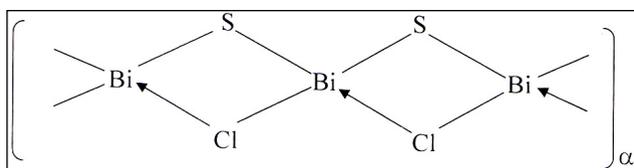
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can be prepared in neutral perchlorate solution. The main product is $[\text{Bi}_6\text{O}_6]^{6+}$ or its hydrated form $[\text{Bi}_6(\text{OH})_{12}]^{6+}$, but at low pH, the products such as $\text{Bi}_2(\text{SO}_4)_3$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ can be obtained. Bi_2O_3 on treatment with nitric acid forms $\text{BiO}(\text{NO}_3)$ and $\text{Bi}_2\text{O}_2(\text{OH})(\text{NO}_3)$. These Bismuthyl salts are generally in soluble in water. But in Bi(III) salt solution having excess of halide ion, it forms complex ion $[\text{BiX}_4]^-$. Moreover, Bismuth hydroxide on treatment with chloride or other strong oxidising agents form bismuthates in alkaline medium. Bismuthates are strong oxidising agent in acidic medium Bi(III) shows six favourable co-ordination state. Bismuth oxyhalides gives typical coordination lattice. They are made from extended sheets with composition $[\text{BiO}]_n$, and are un-neutralized positive charge per metal atoms; between these are inserted double layers of halogen atoms. Bismuth forms a series of mixed oxyhalides with other metal also; with same structural principle like simple oxyhalides. For example BaBiO_2Cl , it is built up of metal oxygen sheet, between which a single layer of halogen atoms exists. But in other compounds, there are a three deep layer of halogen atoms between each pair of metal-oxygen sheets, with a layer of metallic cations at the mid-plane. The cationic layer is generally in completely filled, and so this lead to the formation of compound which do not a simple stoichiometric composition as $\text{Ca}_{1.25}\text{Bi}_{1.5}\text{O}_2\text{Cl}_3$. So, rationally it can't called as mixed crystal.

The compounds like BiSbCl , BiSbBr , BiSI (as also BiSeBr , BiSeI , SbSbr , etc.) which crystallise in rhombic forms, have ribbon like structure, this, ribbon run along the direct of C-axis.



While the compounds BiTeBr and BiTeI crystallise in layer lattices. They do not have tetragonal layer structures, like those of the oxyhalides, but are hexagonal and might be related with the structure of Brucite. The Te and Br or I atoms are distributed in a regular manner the oxygen atom positions of brucite. Bismuth bromide also forms yellow crystal which melts into deep red liquid. Bismuth bromide is easily converted into white oxybromide by water, where as its iodide, due to its low solubility,

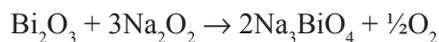
hydrolysed only on boiling. Both, bromide and iodide of Bismuth forms complex salts and other addition compound.

Schumb and Ritter have explained that bismuth trioxide exists in three crystalline states. The insolubility of the bismuth oxides in dilute alkali, as compared with amphoteric oxides of arsenic and antimony, makes it out as being definitely a basic oxide. However, it forms compounds with other metal oxides, when the components are melted together. As it forms the compounds with lead oxides like 2PbO , Bi_2O_3 , $2\text{Pb}_3\text{O}_4$, Bi_2O_3 etc.

Moreover Bismuth hydroxides precipitated by hydroxyl ions from bismuth salt solution as white flocculant substances. This can also be found in colloidal dispersion. Bismuth hydroxides easily dissolves in acids, giving bismuthyl salts, but does not dissolve in dilute alkalis. The existence of two other hydrates $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has been found from the isobaric degradation of the ortho-hydroxide $\text{Bi}(\text{OH})_3$, which may alternatively is bismuth oxide trihydrate.

On the other hand, when the bismuth hydroxide is added in concentrated alkali hydroxide solution and is followed with strong oxidants such as chlorine, Potassium permagnate, Potassium peroxyulphate etc. alkali bismuthates are formed i.e. alkali salt of HBiO_3 in an impure state. Pure bismuthates were obtained as yellow sodium metabismuthate, NaBiO_3 , and brown sodium orthobismuthate Na_3BiO_4 and red or violet Potassium bismuthate.

It was found that sodium bismuthate was more easily prepared by a dry method i.e by heating Bi_2O_3 with sodium peroxide in the molecular proportion of 1:3.



under these condition, the conversion of the bismuth into the pentavalent state takes place. The presence of Bi_2O_3 as an impurity does not interfere the reaction and loss of oxygen easily occurs in the process. The product generally formed must be assumed as mixture of the pentaoxide with Bi_2O .

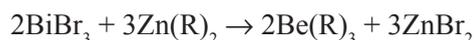
Fluorides of Bismuth i.e. BiF_3 may prepared by treating bismuth oxide with hydrofluoric acid containing the slightly excess of acid which is soluble in conc. Potassium fluoride solution via the

formation of complex salt. Ammonium tetrafluorobismuthate (III) $[\text{NH}_4][\text{BiF}_4]$ was obtained as transparent lustre crystal.

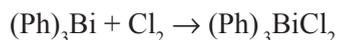
The yellow bismuth thiocyanate $\text{Bi}(\text{SCN})_3$ can be crystallized from solution of bismuth hydroxide in thiocyanic acid. The salt added with alkali thiocyanate to prepared thiocyanato-bismuthate i.e. $\text{M}_3[\text{Bi}(\text{SCN})_6]$. Similarly Bismuth nitrate can be obtained by dissolving bismuth in nitric acid. A crystal with composition $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, crystallise when the solution is evaporated. When these are heated, it loss water and nitric acid, so that bismuthyl nitrate, $\text{BiO}(\text{NO}_3)$ remains.

Bismuth sulphate $\text{Bi}_2(\text{SO}_4)_3$ can be prepared from bismuth or its oxide in concentrated sulphuric acid, where fine white crystal of hygroscopic nature needles obtained. It forms hydrate with even small quantity of water, but hydrolysed to a basic salt to a larger extent. It forms sulphato bismuthates i.e. $\text{K}[\text{Bi}(\text{SO}_4)_2]$ and $\text{K}_3[\text{Bi}(\text{SO}_4)_3]$, on treating with alkali sulphate. If bismuth salt solution is treated with alkali or ammonium carbonates, where basic bismuth carbonate precipitated i.e. $(\text{BiO})_2\text{CO}_3$ (hydrated).

Bismuth alkyls can be obtained by reaction of bismuth bromide with zinc alkyls as :



It can also be prepared as derivative of pentavalent (bismuth e.g.



There are only a few calorimetric reagents known for bismuth. Some of the known. Some of the known reagents proposed for the determination of sodium diethyl dithiocarbamate, ammonium pyrrolidine dithiocarbamate, zinc dibenzyl dithiocarbamate, xylenol orange, Bromo-Pyrogallol red, alizarine red and diphenylguanidine, dithopyrylonethane and electron complexing agent, triethyl tetramine hexacetic acid, diethyl dithiocarbamate – EDTA – KCN, Iodo and rhodamine B, silver diethyl dithiocarbamate, 2-(5-bromo-2-Pyridylazo)-5-diethyl amino phenol.¹⁵

Recently used spectrophotometric reagents are pyrimidine-2-thiol and azosubstituted pyrocatechol.

Liquid – liquid extraction is one of the most popular techniques used for recovery of Bi(III). Earlier, the extraction behaviour of Bismuth(III) was studied using various methods. The 2-bromo-alkanoic acid in benzene and in hexane system were used against the aqueous condition of high acidity for extraction of Bismuth (III). The other prominent reagent used for this purpose include high molecular weight amines (HMWA) and organophosphorous compounds. N-n-Octylaniline and Aliquate 336-S have been used for extraction separation of Bismuth(III) from acetic acid medium. bis(2, 4, 4-trimethyl pentyl) phosphonodithiothionic acid (Cyanex 301), monoctylanilinobenzyl-phosphoric acid, tris(2-ethylhexyl) – phosphate, triphenyl phosphine oxide bis 2,4,4-trimethyl pentyl) monothio phosphinic acid (cyanex 302) are prominent organo-phosphorous extractants used for extraction of Bismuth(III). A study on Bi(III) extraction and its separation from other elements was also carried out with triphenylarsine oxide.

REVIEW OF LITERATURE

N.S. Gill *et al.* has found that Bi(III) forms Bi(III) dithiocarbamates with dithiocarbamate like other metal dithio-carbamates. The unsymmetric mixed ligand dithiocarbamate are by ligand scrambling while mixing with simple symmetrical dithiocarbamate in non-polar solvents. The chemical and spectral analysis revealed that these complexes are identical with those, which derived from halo bis dithio-carbamate.

G. Pyronel *et al.* have reported a number of mixed ligand Bi(III) dithiocarbamate, through halo bis dithiocarbamate of Bi(III). It is found that, even simple mixing of symmetric Bi(III) dithiocarbamate results in the formation of mixed ligand complexes in non-Polar solvents. Moreover Bismuth(III) salt and its complexes. Other research workers have also reported their work.

Recently S.P. Paik, S.K. Ghatak and Kamalika Sen have reported that the extraction and spectrophotometric estimation of Bi(III) and Bi(V) salt in an aqueous polyethylene glycol (PEG) based biphasic system. Na_2SO_4 and MgSO_4 salt rich phase were applied against 50% PEG solution to obtained the two phase system. The chelating ligand, ammonium Pyrrolidine dithiocarbamate (APDC) was used to form a complex with Bi(III)

and Bi(V). These complexes were found to dissolve in aqueous solution of PEG, which can be utilised for spectrometric determination of maximum absorption at 360 nm. The variation of pH of the solution in the acidic range did not affect the extraction efficiency very much and Bismuth can be stripped back in the salt rich phase by the addition of very dilute alkali that breaks the couple, with APDC.

Moreover, Bi(V) compounds of lapachol were found to inhibit the growth of a chronic myelogenous leukemia cell line and this complex was about five times more active than free lapachol. Industry makes use of Bismuth compounds as catalyst in manufacturing acrylonitrile, the starting material for synthetic fibres and rubbers. It has been found that isolation of Bismuth in different chemical form is therefore, a ubiquitous work for analytical chemist.

RESULTS AND DISCUSSION

bis (Salicylaldehyde Pyrrolidine-N-Thiohyrazonato) Bismuth (III) [Bi (SalPyrth) (HSalPyrth)]

Procedure: Bismuth Iodide (2.94 gram, i.e. 0.005 mol) in 50 ml methanol was taken and treated with hot solution of Salicylaldehyde Pyrrolidine-N-Thiohydrazide (2.50 gram in 60 ml methanol) with constant stirring, a yellowish orange precipitate separated out immediately. The precipitate was filtered, washed with methanol and dried in a desiccator over CaCl_2 .

Tri-Iodo (Benzaldehyde Pyrrolidine-N-Thiohydrzone) Bismuth (III) [Bi(HBenzPyrth) I_3]

Procedure : Bismuth Iodide (2.94 gram, i.e. 0.005 mol) in 50 ml. methanol was taken and treated with hot solution of Benzaldehyde Pyrrolidine-N-Thiohydrazide 2.34 gram in 60 ml. methanol) with constant stirring; a orange colour precipitate was separated immediately. The precipitate was filtered, washed with methanol and dried in a desiccator over CaCl_2 .

Iodo-{Bis(Cinnamaldehyde Pyrrolidine-N-Thiohyrazonato)} Bismuth (III) [Bi (CinPyrth) $_2$ I]

Procedure : Bismuth Iodide (2.94 gram i.e. about

0.005 mol in 50 ml methanol) solution was taken and treated slowly with hot solution of Cinnamaldehyde Pyrrolidine-N-Thiohydrazide (about 2.60 gram in 60 ml methanol) with constant stirring, from this reaction mixture, a yellow precipitate separated immediately. The precipitate was allowed to stand for few minutes and filtered, washed with methanol and dried in a desiccator over CaCl_2 .

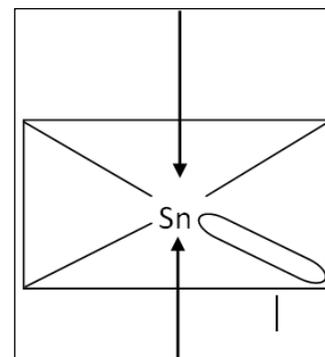
Tri-Iodo(Cyclohexanone Pyrrolidine-N-Thiohyrazone Bismuth(III) [Bi(HcyclPyrth) I_3]

Procedure: Bismuth Iodide (about 2.94 gram i.e. 0.005 mol in 50 ml methanol) solution was taken and treated with hot methanolic solution of cyclohexanone Pyrrolidine-N-Thiohyrazone with constant stirring, a deep orange precipitate was separated immediately. The precipitate was filtered, washed with methanol and dried in a desiccator over CaCl_2 .

The analytical results of the complexes prepared are given in table 1. The solubility of the compounds in different solvents were tested and results are given in the table 2. The qualitative value of molar electrical conductance in D.M.F. solution are given in table-IV.2. The I.R. spectra of some complexes were recorded in the range of $4000\text{-}200\text{ cm}^{-1}$ and their band positions are given in last chapter. The I.R. spectra of the complexes are given in last.

The electronic absorption spectra of ligand and some complexes are given in table 3. The U.V. spectra are given in the last.

Tin, a IVth group element of periodic table. Its general outer electronic configuration is ns^2np^2 and thus for Sn is $5s^25p^2$. As per valency electron Sn shows four valency and thus shows Sn^{+4} oxidation state. Sn can also show Sn^{2+} oxidation state, due to inert pair effect. In the case of +4 oxidation state, Sn shows sp^3 hybridisation and has tetrahedral geometry. In case of Sn^{2+} i.e. $5s^25p^0d^0$ outer electronic configuration, indicates that, Tin in +2 oxidation state has sp^3d^2 hybridisation and thus octahedral geometry. But due to



Triangular Pyramidal Shape

Table 1: Analytical Results

Complex	% of Carbon		% of Hydrogen		% of Nitrogen		% of Sulphur		% of Iodine		% of Metal	
	Found	Calc.	Found	Calc.	Found	Found	Calc.	Calc.	Found	Calc.	Found	Calc.
[Bi(SalPyrth) (HSalPyrth)]	40.81	40.88	3.82	3.87	11.89	11.93	9.06	9.09	–	–	29.62	29.66
[Bi(HBenzPyrth) ₃]	17.49	17.52	1.81	1.83	5.08	5.11	3.85	3.89	46.22	46.25	25.34	25.40
[Sb(CinPyrth) ₂ I]	39.41	39.45	3.72	3.77	9.82	9.87	7.49	7.53	14.84	14.87	24.48	24.52
[Bi(HCyclPyrth) ₃]	16.21	16.22	2.32	2.35	5.11	5.16	3.89	3.94	46.70	46.72	25.60	25.65

Table 2: Solubility of complexes in different solvents and their electrical conductivity

Complexes	Colour	Methanol	Benzene	Chloroform	D.M.F	λ	α
						mol ⁻¹ ohm ⁻¹ cm ² in D.M.F	
Bi(SalPyrth) (HSalPyrth)	Yellowish orange	F.S	S.I.S	S.I.S	S	3	
Bi(HBenzPyrth) ₃	Orange	S.I.S	S.I.S	F.S	H.S.	12	
Bi(CinPyrth) ₂ I	Yellow	S.I.S	S.I.S	S.I.S	H.S	7	
Bi(HCyclPyrth) ₃	Deep Orange	S.I.S	F.S	F.S	S	13	

N.B.: S–Soluble; S.I.S.–Slightly Soluble; F.S–Fairly soluble; S.–Highly soluble.

Table 3: Electronic absorption spectral band position of ligands and complexes with their tentative assignments

Compound	Electronic bond positions in nm (ϵ_{Max} in molar)		Assignment
HBenzPyrth	290	sh	n \rightarrow π
	312	sh.	$\pi \rightarrow \pi^*$
HBenzPyrth	312	st.	n \rightarrow π
	390	w	$\pi \rightarrow \pi^*$

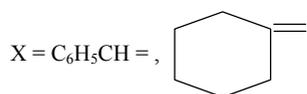
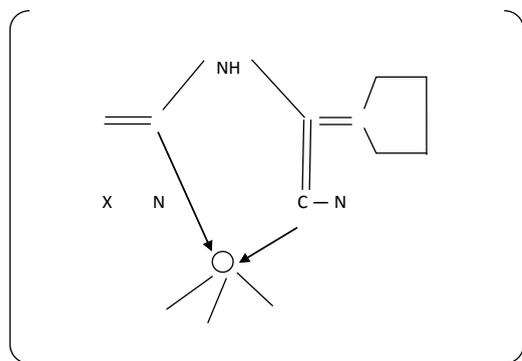
N.B. – sh.–shoulder; st.–strong; w–weak.

presence of lone pair of electron, it forms triangular pyramidal shape as below :

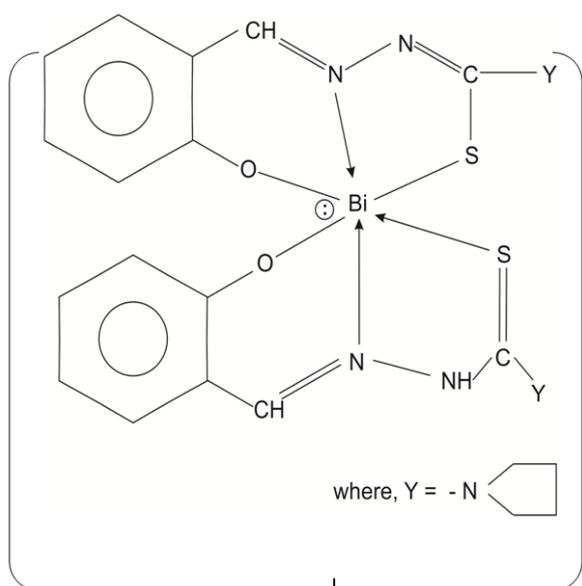
The halides of Bismuth i.e. Bismuth chloride and bromide are very susceptible to hydrolysis forming Biox and therefore attempt to prepare BiCl₃ or BiBr₃ complexes in presence of air and absolute ethanol or methanol gives impure product. However, BiI₃ is quite stable and it remains stable in methanol or ethanol for hours. The interaction of BiI₃ with ligand molecule at reflux temperature gives three types of complexes of formular [BiL₂I] (HL = HcinPyrth) and [Bi(LH)₃] (LH = HBenzPyrth, HCyclPyrth) and [Bi(LH)L] where (LH₂ = H₂SalPyrth).

The complexes are fairly stable at room temperature for long time and do not loss weight below 138°C – 170°C. In some complex very slow loss in weight starts above 160°C – 170°C. So the complexes do not have sharp melting point. The complexes dissolves in methanol, benzene, ethanol, chloroform, dioxan, D.M.F. to a variable extent. In general,

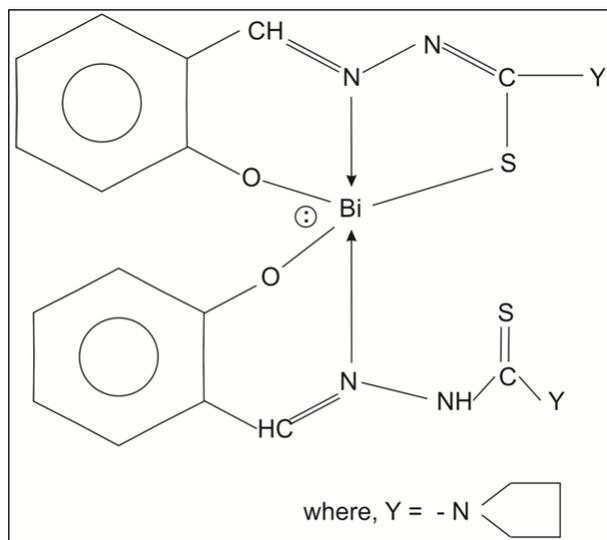
cyclohexan none complexes have fair solubility while cinnamaldehyde schiff base complexes have poor solubility. The neutral inner complexes of salicylaldehyde thiohydrazone have lower solubility in benzene but highly soluble in D.M.F. The solubility of complexes in dioxane and D.M.F. are relatively high. The electrical conductance value of complexes in D.M.F. at room temperature has been recorded and found in the range of 3-13 ohm⁻¹ mol⁻² cm². The negligible electrical conductance value of complexes indicates their non-ionic character. The solubility of these complexes in different organic solvents suggest that, these complexes are not polymeric metal complexes. Since Pyrrolidine being the strong base and possessing high electron pushing character so, the ligand is not deprotonated in similar experimental condition in case of salicylaldehyde schiff base, one of the ligand molecule is bonded metal atom as dianionic molecule while the other as mono anionic group.



Structure of [Bi(LH)L] type of complexes where, (H₂L = H₂SalPyrth)



Or



CONCLUSION

In general, it has been found that Bismuth appears to be surrounded by five donor atom in complexes of the [BiL₂] and [Bi(LH)I₃], but probably, it is hexa coordinated with salicylaldehyde thiohydrazone. Though electronic spectra of ligands and some of its complexes has been recorded, but electronic absorption band position do not provide significant information regarding structure of non-transition metal complexes. It has been found that electronic absorption bands are affected significantly in complexes indicating its coordination with metal atoms (Table 3). A strong band observed in the absorption spectra of the complexes in the region, 390-425 nm, which is not present in free ligand, which attributed to charge-transfer band from (Bi-I) bond. The I.R. spectral analysis has indicated the bidentate N-S donor sites of thiohydrazone, but it is tridentate (i.e. N, O, S) donor sites in case of salicylaldehyde-N-thiohydrazone. The I.R. spectra results will be explain in detail in the last (V) chapter. Hence, on the basis of stioichiometry and other physico-chemical analytical evidences, the following structure can be suggested for the complexes of Bismuth. Structure of [Bi(LH)I₃] type of complexes, where (LH = HBenzPyrth, HCyclPyrth, etc.)

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