INTRODUCTION OF SELENOSEMICARBAZONE

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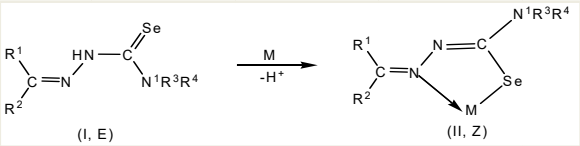
Abstract - This paper is designed to explain the introduction of selenosemicarbazone. Selenosemicarbazones are schiff bases characterized by the presence of selenium and azomethine nitrogen offering a ready co-ordination site due to the presence of a lone pair of electrons on these donor atoms. Selenosemicarbazone can adopt a variety of different coordination modes. selenosemicarbazone and their complexes showed good biological activity such as antifungal , antiparasitic , antibacterial , antimalarial , anticancer , anti-oxidant, anti-proliferative , anti-angiogenic and antidiabetic activity .

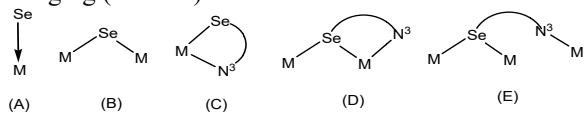
Keywords - Selenosemicarbazone, Co-ordination, Biological activity.

I. INTRODUCTION

Selenosemicarbazones are the selenium analogue of thiosemicarbazaones. In neutral form, a selenosemicarbazone exists in E-mode (I) and binds to metal centre via selenium atom, however, on deprotonation of hydrazine N^2H hydrogen, it change to Z mode (II) and form a chelate ring.



Selenosemicarbazone can adopt a variety of different coordination modes. Selenosemicarbazone coordinate as bidentate ligands via azomethine nitrogen and thione/thiol to selenium. When additional coordination functionality is present in the proximity of donating centres, the ligands will coordinate in a tridentate manner. Various bonding modes of selenosemicarbazones are: i) selenium bonded terminally, η^1-Se (mode A) (ii) (mode D) ; v) Se-selenium atom bridges two metal centers, μ-Se (mode B) ; iii) chelation by N, Se- (mode C) ; iv) chelation by N, Se- cum-Se-bridging bridging-cum-Se, N-bridging (mode E) .



Apart from structural diversity and variable bonding modes, the biological properties of selenosemicarbazones are often related to metal ion coordination. The metal complex can be more active than the free ligand. Some of the synthesized selenosemicarbazone and their complexes showed good biological activity such as antifungal, antiparasitic , antibacterial , antimalarial , anticancer, anti-oxidant, anti-proliferative , anti-angiogenic and antidiabetic activity. Even some of the comparative studies explained that selenosemicarbazones showed similar or although better biological activities than the corresponding thiosemicarbazones and their complexes while oxygen analogues showed the lower activity.

Selenosemicarbazones can be prepared by various methods. Brief description of these methods is given below:

❖ **Method-** Selenosemicarbazones can be prepared by direct condensation of aldehyde or ketone with selenosemicarbazide in methanol

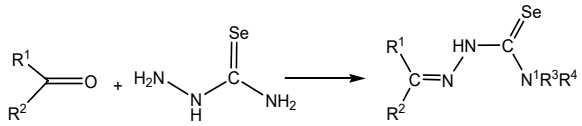


Chart 1

❖ **Method-** Reaction of hydrazine hydrate with KSeCN and aldehye / ketone in acidic medium resulted into respective selenosemicarbazone

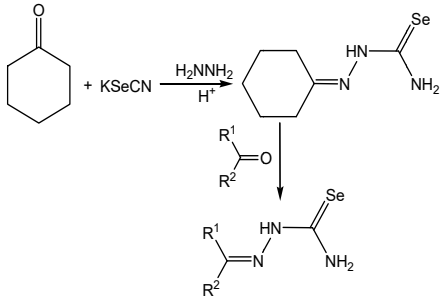


Chart 2

❖ **Method-**

Selensemicarazones can also be prepared by replacement of sulfur by selenium in thiosemicarbazones. Thiosemicarbazone was first methylated by reacting it with methyl iodide (CH_3I) and then treated with sodium hydride selenide and $NaBH_4$ under inert atmosphere to give corresponding selenosemicarbazone

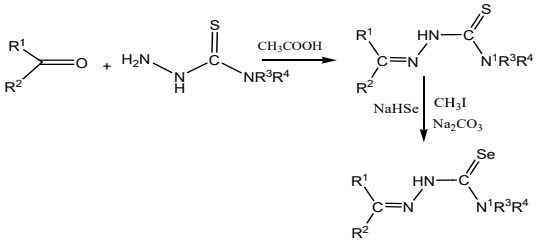


Chart 3

❖ **Method-**

Not only sulfur, oxygen of semicarbazone can also be replaced by selenium to form selenosemicarbazone**.** In this method, PCl_5 was added to a solution of semicarbazide in dry CH_2Cl_2 at 0°C and then reacted with a freshly prepare THF solution of LiAlHSeH

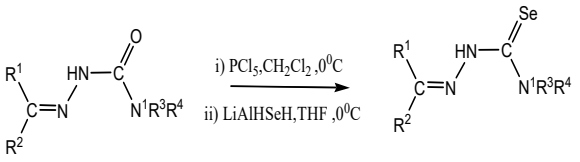
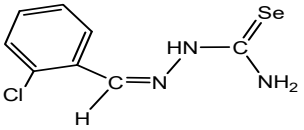


Chart 4

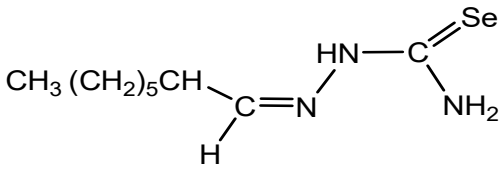
II. LITERATURE SURVEY

A number of selenosemiarbazones has been reported in literature. Depending on the substituent at C^2 carbon and number of selnosemicarbazone moiety, these ligands are divided into following categories -

- **Selenosemicarbazones with un-substituted and substituted aromatic ring at C^2 carbon-** Selenosemicarbazones with mono-substituted, di-substituted and tri-substituted benzene rings are known. Halogens, methyl group, hydroxyl, diphosphines etc. are present at ortho- or meta- or para- positions of benzene ring. Example

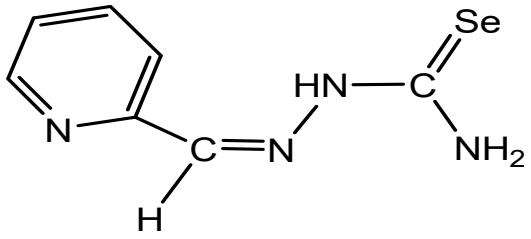


- **Selenosemicarbazones with aliphatic chain at C^2 carbon-** Selenosemicarbazones with aliphatic chains having carbon atom ranging from 3 to 10 at C^2 carbon. Example



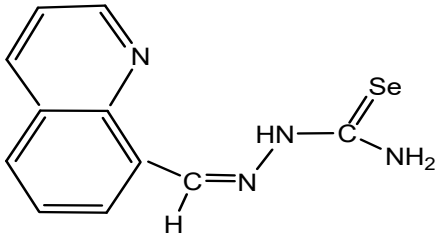
- **Selenosemicarbazones with heterocyclic ring at C^2 carbon-**

Selenosemicarbazones with un-substituted and substituted pyridine ring at C^2 carbon are well known. With five membered heterocyclic ring, a few selenosemicarbazones are formed for example thiophen-2-carbaldehyde selenosemicarbazone, thiazol-4-carbaldehyde selenosemicarbazone, where two heteroatoms are present in the ring is also known. Example

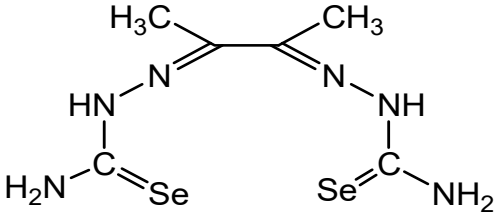


- **Selenosemicarbazones with fused ring at C^2 carbon-**

Few selenosemicarbazones with fused ring at C^2 carbon are also known. Fused ring in these ligands is either aromatic or one aromatic and one heretocyclic. Example



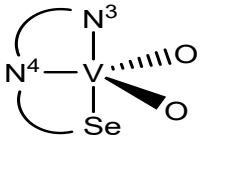
- **Bis-Selenosemicarbazones at C^2 carbon-** Selenosemicarbazones, where two arms are connected via a ring or a C–C bond are reported. Example



III. COMPLEXES OF SELENOSEMICARBAZONES

A large number of complexes of thiosemicarbazones with d-block elements are known but only few complexes of selenosemicarbazones are reported till date and brief description is given as –

Vanadium and Cobalt: V(II) reacted with 2-acetylpyridine N,N- dimethylselenosemicarbazone (HLSe) to form complexes of stiochiometry, $[V(O)_2(LSe)]$ **1** and $[VO(acac)(LSe)]$ **2**. Complex **1** has distorted trigonal bipyramidal geometry, whereas complex **2** is octahedral. In complex **1**, pyridine nitrogen atom and selenium atom lied on axial position and two oxygen atoms from oxo ligands and imine nitrogen atom were present in the triangular base. In these complexes, selenosemicarbazone bind via N, N, Se- donor atoms and act as monanionic tridentate ligand.



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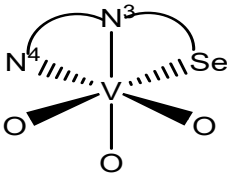

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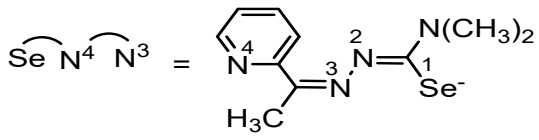
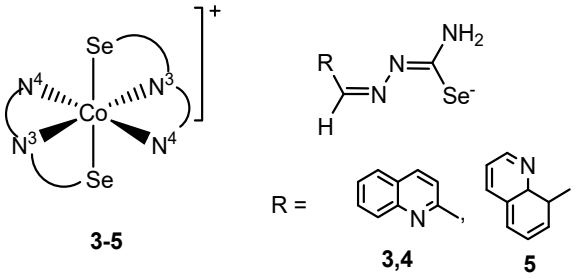
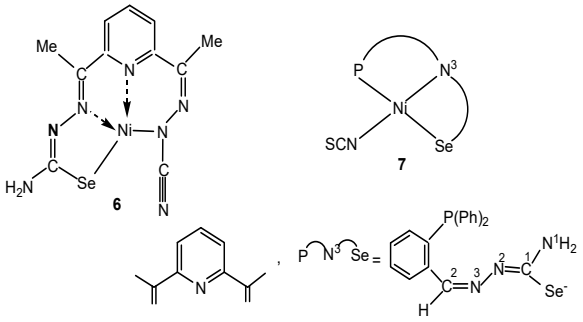


2-quinolinecarboxaldehyde selenosemicarbazone (Hqasesc) and 8-quinolinecarboxaldehyde selenosemicarbazone (Hqasesc)reacted with cobalt (II) to complexes of stiochiometry, $[Co(2qasesc)_2]X.H_2O$ (X= ClO_4^- **3**; BF_4^- **4**) and $[Co(8qasesc)_2]ClO_4$ **5** respectively. Geometry around cobalt is octahedral in all these complexes.



Nickel, Platinum and Palladium:

When the ligand 2,6-diacetylpyridine-bis(selenosemicarbazone)(H_2L) was reacted with $Ni(OAc)\cdot 4H_2O$, a part of side chain of symmetrical ligand was modified to 2-{1-[6-(1-selenosemicarbazonoethyl)-2-pyridyl]ethylidene} hydrazine carbonitrile with evolution of hydrogen selenide resulting in the formation of complex, [Ni(L)] **6**, 2-(diphenylphosphino)benzaldehyde selenosemicarbazone (HL) formed a diamagnetic complex, [Ni(L)(NCS)] **7** [35, 48]. Both the complexes exhibited square planer geometry with ligand binding via hydrazinic nitrogen, selenium and heteroatom of the ring.

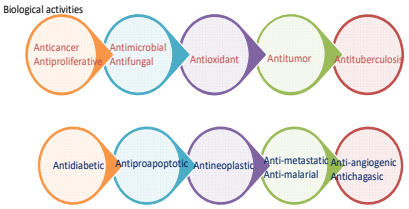


Ni(II) reacted also with 2-quinolinecarbaxaldehyde (Hqasesc) to form complex of stiochiometry, $[Ni(qasesc)_2]$ **8** [43]. Geometry around nickel is octahedral in complex **8.**

IV. BIOLOGICAL APPLICATIONS OF SELENOSEMICARBAZONES

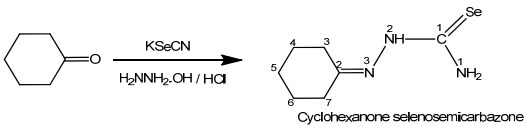
Importance of selenosemicarbazones and their complexes lies in their vide range of biological activities. These **activities** includes anticancer, Antiproliferative, Antibacterial, Antioxidant, Antitumor, Antituberculosis and antidiabetic, Anti-proapoptotic and Antineoplastic, Antimicrobial, Anti-metastatic, Anti-malarial, Anti-angiogenic, Anti-fungal, Antichagasic etc**.**

Biological applications of selenosemicarbazones and their complexes:

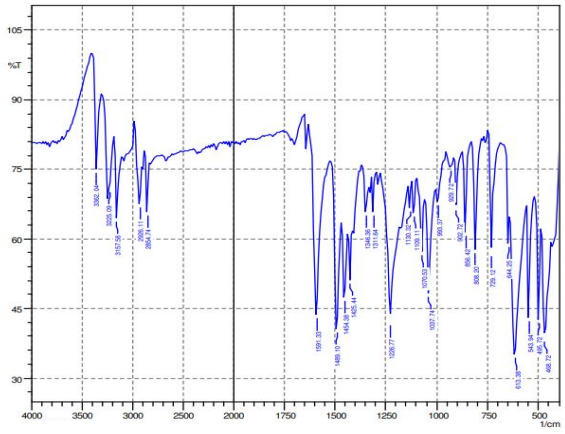


V. CONCLUSION

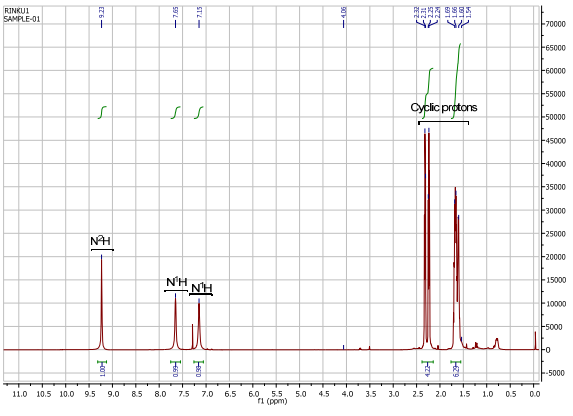
Synthesis of Cyclohexanoneselenosemicarbazone



IR of Cyclohexanoneselenosemicarbazone



NMR of Cyclohexanoneselenosemicarbazone



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