

Studies On The Complexes of 1,1^L-BIS (Seleno Cyanato Mercurio) Ferrocene with Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV) Chlorides

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Abstract

The multi nuclear complexes involving Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV) chlorides with ferrocene derivative has not been reported nor any effort has been made to synthesize such complexes. Silicon (IV), tin(IV), titanium(IV), Zirconium(IV) and Hofnium(IV) from 1:1 and 1:2 adducts with number of monodentate & bidentate ligands[1-5]. No attempt has been made to react ferrocene derivative with these tetravalent lewis acids. In recent years ferrocene derivatives have been used as bases[6-7] towards certain metal ions but not towards group four tetrachlorides. The multinuclear complexes have been synthesized by following strict dry conditions using dry box flushed with nitrogen. In the process of synthesis of the complexes, the ferrocene derivatives, which was used as ligand was prepared by the following method. The 1,1^L-Bis (thio/selenocyanate) was reacted with MCl₄ [M=Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)]. By adopting this procedure the following complexes were prepared. They have been referred to as tetrachloro adducts.

Ligand: 1. Fe(C₅H₄HgSCN)₂;

2. Fe(C₅H₄HgSeCN)₂

List of tetrachloro adducts:

1. Fe(C₅H₄HgSCN)₂SiCl₄;

2. Fe(C₅H₄HgSCN)₂SnCl₄;

3. Fe(C₅H₄HgSCN)₂TiCl₄;

4. Fe(C₅H₄HgSCN)₂ZrCl₄;

5. Fe(C₅H₄HgSCN)₂HfCl₄;

6. Fe(C₅H₄HgSeCN)₂SiCl₄;

7. Fe(C₅H₄HgSeCN)₂SnCl₄;

8. Fe(C₅H₄HgSeCN)₂TiCl₄;

9. Fe(C₅H₄HgSeCN)₂ZrCl₄;

10. Fe(C₅H₄HgSeCN)₂HfCl₄.

The hexathio/selenocyanate complexes prepared are listed below:

List of hexathio/Selenocyanate adducts:

1. Fe(C₅H₄Hg)₂ Si(NCS)₆;

2. Fe(C₅H₄Hg)₂ Sn(NCS)₆;

3. Fe(C₅H₄Hg)₂ Ti(NCS)₆;

4. Fe(C₅H₄Hg)₂ Zr(NCS)₆;

5. Fe(C₅H₄Hg)₂ Hf(NCS)₆;

6. Fe(C₅H₄Hg)₂ Si(NCSe)₆;

7. Fe(C₅H₄Hg)₂ Sn(NCSe)₆;

8. Fe(C₅H₄Hg)₂ Ti(NCSe)₆;

9. Fe(C₅H₄Hg)₂ Zr(NCSe)₆;

10. Fe(C₅H₄Hg)₂ Hf(NCSe)₆.

Keywords: Seleno Cyanato Mercurio, Ferrocene and Tetrachlorides.

Introduction

Organometallic chemistry is of growing interest especially in the recent decades due to its wide applications in the biological and medicinal field, this application leads to a new area called bioorganometallic chemistry. Ferrocene moiety is used in bioorganometallic chemistry due to its stability, biological activity and application in organic synthesis to prepare new compounds. Also, metal complexes are used in bioorganometallic chemistry since they exhibit a wide range of biological

activities against various diseases. Since the discovery of ferrocene 1 in 1951 [8], ferrocene and its derivatives have attracted the attention of many researchers in the field of organometallic chemistry for using in various applications such as materials science [9-10], bio-organometallic and biological chemistry [11-13], nonlinear optics [14], asymmetric catalysis [15], polymer science as redox active polymers [16-17], electrochemistry [18-19], corrosion inhibition [20] and molecular recognition as biosensors [21-23]. Many ferrocene compounds display interesting antibacterial [24], antifungal [25], antimalarial [26-27], antitumor [28-29], antioxidant [30] and cytotoxic [31-32] activities. Also, ferrocene compounds appeared promising in biological activities. For example, ferroquine 2 (FQ, SR97193), is a new antimalarial [33]. Compound 3 is a potent antifungal agent and showed 100% inhibitory ratios against *S. sclerotiorum*, *P. oryzae* and *C. cucumerinum*. Compound 4, [34]3-ferrocenoyl-1-(4-trifluoromethoxyphenyl) urea, shows a potential in vitro antitumor activity using reported method [35] against cervical carcinoma cells (KB cells) [36] and compound 5, 1-(4-chlorophenyl)-3-ferrocenylurea, showed potential anti-HIV protease activity [37].

Objectives of the Study

1. Studies on the complexes of 1,1'-bis ferrocene with $si(iv)$, $sn(iv)$, $ti(iv)$, $zr(iv)$ and $hf(iv)$ chlorides.
2. Infrared studies of complexes.

Review of Literature

A few complexes of copper(II), nickel(II), cobalt(II), Zinc(II), tin(IV) and cadmium(II) with two newly synthesized organometallic compounds, 1-Formylferrocene phenyl-N-thiosemicarbazone (HFfptsc) and 1-acetyl ferrocene phenyl N-thiosemicarbazone (HAfptsc) have been isolated. The interaction of (HFfptsc) with Me_2SnCl_2 and $MeSnCl_3$. Yield a series of organotin (IV) compounds. The reactivity of $MeSn(Ffptsc)_2Cl$ towards $MeSH$, Me_2N , $SiMe_3$, Me_2NsiMe_3 , $SiMe_3N_3$, and $Me_3SiC\equiv C-Ph$ are also described. These complexes have been characterized on the basis of elemental analysis, molecular weights, molar conductances, magnetic moments and spectroscopic (IR, ^1H-NMR , UV-vis) data⁽⁴⁴⁾. Lanthanide(III), Cerium(III), Praseodymium(III), neodymium(III), Samarium(III), gadolinium(III), terbium(III), dysprosium(III) and yttrium(III) complexes of Schiff bases derived from ferrocenyl keto acid and 2-quinolonyl hydrazine (H_2L) and Ferrocenyl keto acid and 8-quinolonyl hydrazine (H_2L^1) have been prepared. The complexes are of the type $[Ln(HL)L](H_2O)_n$, $[Ln(HL^1)L^1](H_2O)_n$ ($n=1-2$) and $[Ln(HL^1)L^1]$ and these have been characterized on the basis of elemental analysis, conductance measurements. Magnetic moments thermal analysis, infrared and electronic absorption spectra. Nephelauxetic ratio (β) and covalency factor ($b_1/2$) have been determined for neodymium(III) complexes, which indicate some covalent character in these complexes⁽³⁴⁾. Schiff bases and their complexes are versatile compounds synthesized from the condensation of an amino compound with carbonyl compounds and widely used for industrial purposes

and also exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. A few ferrocenyl Schiff bases have been isolated by the condensation of Formyl ferrocene and acetyl ferrocene with 4methyl ortho phenylene diamine, orthoamino naphthol and ortho- amino naphthoic acid. Reactions of these ferrocenyl Schiff bases with copper(II) cobalt(II) and nickel(II) salts in varied reaction conditions, Yield new complexes of the type $M(L)_2$ and also some mixed ligand complexes of the type $M(L)(X)(NH_3)$ (where HL is mono basic bidentate ferrocenyl Schiff base, $M=Ni(II)$, $Cu(II)$, $Co(II)$ and $X=(OH/Cl)$). Cobalt (III) complexes of the type $Co(L)_2(OH)(NH_3)$ are also isolated. The compounds have been characterized on the basis of elemental analysis, molar conductance, molecular weights, magnetic susceptibilities and spectroscopic (Electronic and infrared) data⁽⁴⁶⁾.

Experimental

Material and Manipulations

Reagent grade solvent were purified and dried before use. Metal tetrachlorides, MCl_4 [$M=Si(IV)$, $Sn(IV)$, $Ti(IV)$, $Zr(IV)$ and $Hf(IV)$] and ferrocene were procured from BDH/Aldrich and used under strict dry conditions from fresh, bottles. Potassium selenocyanate and 1,1'-bis (seleno cyanatomercurio) ferrocene were prepared as below:

Preparation of potassium selenocyanate

Potassium selenocyanate was prepared by following reported method.⁽³⁸⁾

A mixture of 120 gm. Commercial grey selenium metal and 105 gm. Potassium cyanide was melted in a large porcelain dish at $160^\circ C$. The melt was stirred continuously with a porcelain spatula until all the selenium dissolved and the melt became transparent. The melt was cooled with continuous stirring and the cooled melt was crushed to fine powder and dissolved in hot acetone. A slow stream of carbon dioxide dried over phosphorus pentoxide (P_2O_5), was bubbled into the solution for two hours and filtered through a buchner funnel. The filtrate was transferred to a distilling flask, and two third of acetone was distilled off. The residual solution was poured into a beaker and cooled. Potassium selenocyanate crystallized out as colourless needles which was filtered, washed with anhydrous ether and dried in vacuum desiccators. The purity of the compound was tested by elemental analysis and infrared spectral measurements.

Anal: Calc. Se = 58.80% found Se = 58.02%

I.R.: $\nu(C-N)=2083, 2071, 2030\text{ cm}^{-1}$; $\nu(C-Se)=559\text{ cm}^{-1}$; $\delta(\text{Se CN}) = 417\text{ cm}^{-1}$

Preparation of 1,1'-Bis (selenocyanato mercurio) ferrocene

To a solution of 18.4 gm (.1 mol) of ferrocene in 96 ml benzene, a solution of 32.8 gm (.1 mol) of mercuric acetate in 360 ml. methanol, was added dropwise over a period of one hour with continuous stirring. To this solution 14.4 gms (0.1mol) of potassium selenocyanate in 15 ml. of distilled water was added and stirred for half hour. An orange yellow precipitate was obtained which was filtered through Buchner funnel, washed with petroleum ether and dried in vacuum. This compound was a mixture of

ferrocenyl mercury(II) selenocyanate and ferrocenylene bis [Mercury(II) Selenocyanate]. From this mixture ferrocenyl bis [Mercury (II) selenocyanate) was separated by soxhlet extraction using 1,2-dichloro ethane. On vacuum evaporation of the extract ferrocenyl mercury(II) selenocyanate was obtained. The residue was purified by dissolving in dimethyl sulphoxide (DMSO), followed by addition of water. The purity of the compound was tested by elemental analyses and IR spectral measurements. The ligand so obtained used in complex formation. The purity of the compound was tested by elemental analysis and infrared spectral measurements.

Anal.: Nitrogen % Selenium% Mercury%
Cal.: 3.53 19.89 50.12
Found: 3.50 19.78 49.48

m.p. = 122°C (d),

Colour = Yellow.,

Solubility = Dimethyl sulphoxide

I.R. spectral positions:

Found: $\nu(\text{C-N})$, 2180(S), 2130(S), 2080(Sh) cm^{-1}

$\nu(\text{C-Se})$ 820(S), 510(S) cm^{-1}

$\delta(\text{N-CSe})$ 480(S), 480(S) cm^{-1}

Solution phase: $\nu(\text{C-N})$ 2130(S), 2070(S) cm^{-1}

$\nu(\text{C-Se})$ 760(S), 740(S) cm^{-1}

$\delta(\text{NcSe})$ 440(S) cm^{-1}

Preparation of $[\text{Fe}(\text{C}_5\text{H}_4\text{HgSeCN})_2 \text{MCl}_4] \text{M} = \text{Si(IV), Sn(IV), Ti(IV)}$

A homogeneous suspension of 7.9 gm (.01 mol) of 1,1-Bis(seleno cyanato mercurio) ferrocene was prepared in 100 ml of dried carbon tetrachloride. The suspension was placed in a three necked round bottom flask, with arrangement of continuous stirring through a Teflon coated magnetic bar. A solution of 1.17 (.01mol) of tin tetrachloride in 100 ml dry carbon tetrachloride was filled to one of the necks of the three necked flask. The second neck was provided with inlet of nitrogen and the third for exit through a calcium chloride tube. The tin tetra chloride solution was slowly added with continuous stirring. After the complete addition the separating funnel was replaced by leibig condenser and a clear solution was obtained. Turbidity if any was removed and the solution was further stirred for another 12 hours. A precipitate appeared which was filtered off washed with solvent and dried in vacuum. The whole procedure was carried out in strict dry condition in a dry box flushed with nitrogen. Silicon and titanium tetrachloride, were similarly reacted and the respective complexes prepared, yield 60%. The tetrachlorides of zirconium and hafnium which were not soluble in carbon tetrachlorides, were reacted in suspension phase and prepared in similar manner as that of tin complexes.

Analysis of the complexes

The complexes were, gravimetrically⁽³⁹⁾ analysed for sulphur as barium sulphate, chloride as silver chloride, mercury as mercury⁽⁴⁰⁾ sulphide, selenium as selenium metal, metals (Sn, Ti, Zr and Hf) by simple gravimetric methods. And nitrogen by semimicro kjeldhal methods. The results of all the analysis are presented in the table 2.

The molar conductance was measured in dimethyl sulphoxide (DMSO), using a Toshniwal conductivity bridge. The infrared spectra was

recorded as nujull mulls on Pye Unicam SP-3-300 spectrophotometer in the range of 4000-200 cm^{-1} , these are presented in table 3.

Results and Discussion

In 1,1-Bis (thiocyanato mercurio) ferrocene it was noticed that in solid phase the compound is in dimer state and in solution phase it is monomer. The selenocyanate analogue has also been examined for the same.

Table A. I.R. spectral bands positions in 1,1-Bis (selenocyanato mercurio) ferrocene (cm^{-1}):

	$\nu(\text{C-N})$	$\nu(\text{C-Se})$	$\delta(\text{NCSe})$
Solid phase	2180(s)	820(s)	480(s)
	2130(s)	510(s)	
	2080(sh)		
Solution phase	2130(s)	760(s)	440(s)
	2070(s)	740(s)	

The infrared spectra of the selenocyanate analogue (FBMS) in solid and solution phase show differences in number of peaks in $\nu(\text{C-N})$ region like their thiocyanate counter parts as described. The solid phase spectra has an additional peak at 2180 cm^{-1} , which is absent in solution phase.⁽⁴¹⁾ This is due to the dimeric nature of 1,1-Bis (selenocyanato mercurio) ferrocene in solid phase and monomeric in solution phase. Further it has been reported that CH_3HgSCN also exist in dimeric nature in solid phase and monomeric in solution phase. For deriving any shift we have used, the position of various peaks in solution spectra.⁽⁴²⁾

Adducts $[\text{C}_5\text{H}_4\text{Hg SeCN}]_2 \text{FeMCl}_4 [\text{M} = \text{Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)}$

Silicon, tin, titanium, zirconium and hafnium, the group four elements of periodic table has $(n-1) d^2, ns^2$ outer electronic configurations. They forms halides of the type MX_4 [where $\text{X} = \text{Cl}^-, \text{Br}^-$ and I^-]. In MCl_4 the co-ordination number of M is four which can raise to six, since they can raise their co-ordination number, they acts as acceptors.⁽⁴³⁾ On reacting with $[\text{C}_5\text{H}_4\text{Hg SeCN}]_2$ they form adduct of general formula $[\text{C}_5\text{H}_4\text{Hg SeCN}]_2 \text{MCl}_4$ and raise the co-ordination number to six around M. MCl_4 . acts as lewis acid has a vacancy to accept two lone pairs of electrons donated by 1,1-Bis (Selenocyanato mercurio) ferrocene.⁽⁴⁴⁾

The molar conductance values of the complexes in dimethyl sulphoxide as presented in Table 1, show that the complexes are non-conducting in nature. All are insoluble in common organic solvents like benzene, hexane, ether, alcohol, nitrobenzene, dioxane, dimethyl formamide but soluble in dimethyl sulphoxide.

A reference to Table 3 shows that band positions in IR spectra changed significantly in adducts. The comparison of the spectra of ligand and the adduct shows that there is a positive shift in the $\nu(\text{C-N})$ stretching frequency. Which are in the range of bridging thiocyanate group.⁽⁴⁵⁻⁴⁸⁾

A reference to Table 3 shows that the selenocyanate of 1,1-Bis (selenocyanato mercurio) ferrocene has coordinated through its free nitrogen end to M of MCl_4 . The position of $\nu(\text{C-N})$, $\nu(\text{C-Se})$

and $\delta(\text{NCSe})$ clearly show that only nitrogen bonded selenocyanate is present in these complexes.⁽⁴⁹⁻⁵²⁾

The infrared spectral analysis coupled with analytical results, molar conductance and magnetic moment help in determining the composition. On the basis of these results the structure for the adducts are as shown in Fig. 2.

Comparison between thio and selenocyanate series

Both thio and selenocyanate series of adducts are basically similar in their structure and property but they differ in following respect.⁽⁵³⁻⁵⁷⁾

1. The adducts of 1,1'-Bis (thiocyanatomercurio) ferrocene are more stable in comparison to their selenocyanate analogue. On standing

selenocyanate adducts gets decomposed liberating selenium metal, while thiocyanate analogues can be stored for few months without decomposition.

2. The molar conductance values of selenocyanate series of complexes are slightly lower than those of thiocyanate analogue, indicating that their dissociation in solution is less.
3. The complexes of thiocyanate group are more soluble in dimethyl sulphoxide than those of selenocyanate group.
4. The bands assigned to $\delta(\text{M-NCSe})$ in the lewis acid appear at lower frequency as compared to $\delta(\text{M-NCS})$ bands.

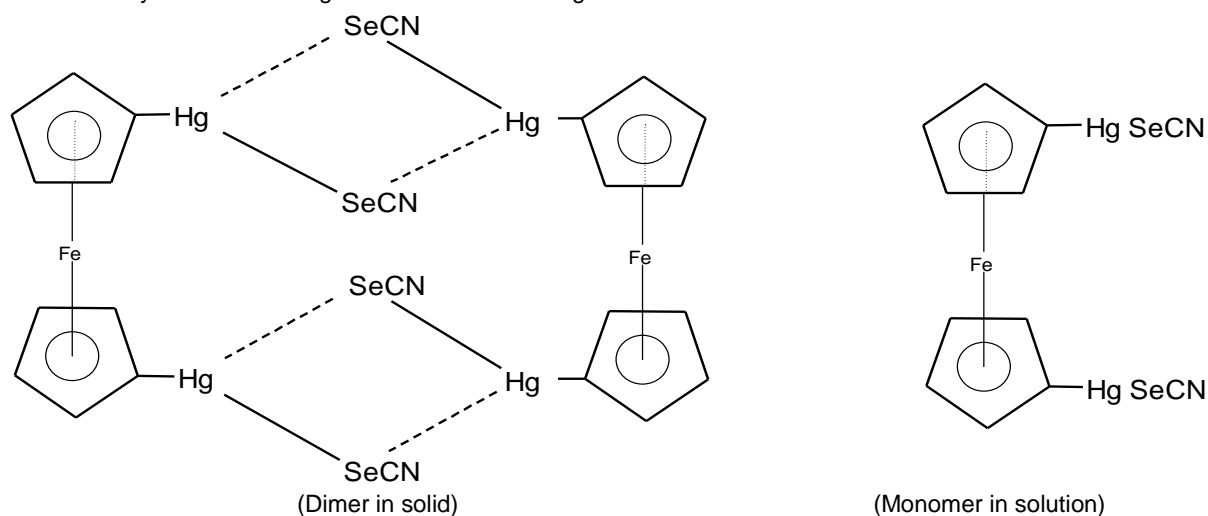


Fig. 1

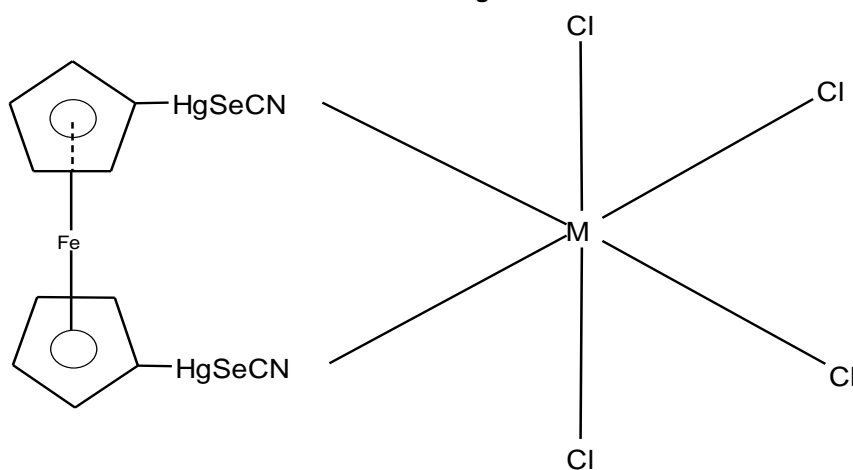


Fig. 2

Table - 1
Physical Measurements

S.No.	Complexes	Colour	Yield %	M.P. °C	^a Molar Cond. (in DMSO cm ² mol ⁻¹)
1.	[Fe(C ₅ H ₄ HgSeCN) ₂ SiCl ₄]	Dark green	64	95	25.39
2.	[Fe(C ₅ H ₄ HgSeCN) ₂ SnCl ₄]	Dark green	68	280d	21.50
3.	[Fe(C ₅ H ₄ HgSeCN) ₂ TiCl ₄]	Dark green	65	75	21.18
4.	[Fe(C ₅ H ₄ HgSeCN) ₂ ZrCl ₄]	Light green	62	182	20.74
5.	[Fe(C ₅ H ₄ HgSeCN) ₂ HfCl ₄]	Steel grey	66	260	28.76

d=decomposition

Table – 2
Analytical Data of The Complexes

S.No.	Complexes	N%		Se%		Cl%		Hg%		M%	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1.	[Fe(C ₅ H ₄ HgSeCN) ₂ SiCl ₄]	2.90	2.86	16.37	16.28	14.73	14.70	41.57	41.0	–	–
2.	[Fe(C ₅ H ₄ HgSeCN) ₂ SnCl ₄]	2.65	2.60	14.96	14.82	13.46	13.38	38.00	37.82	11.24	11.05
3.	[Fe(C ₅ H ₄ HgSeCN) ₂ TiCl ₄]	2.84	2.72	16.04	16.00	14.43	14.40	40.75	40.60	4.86	4.68
4.	[Fe(C ₅ H ₄ HgSeCN) ₂ ZrCl ₄]	2.72	2.68	15.36	15.28	13.82	13.62	39.01	38.85	8.86	8.72
5.	[Fe(C ₅ H ₄ HgSeCN) ₂ HfCl ₄]	2.51	2.48	14.16	14.12	12.73	12.60	35.96	35.80	16.01	15.98

Table 3
Infrared Spectral Band Assignments of The Complexes

S.No.	Complexes	$\nu(\text{C-N})$	$\nu(\text{C-X})$	$\delta(\text{NCX})$
1.	[Fe(C ₅ H ₄ HgSeCN) ₂ SiCl ₄]	2120(s)	735(s), 755(w)	460(s), 410(s)
2.	[Fe(C ₅ H ₄ HgSeCN) ₂ SnCl ₄]	2145(s)	720(s), 760(w)	420(s), 460(m)
3.	[Fe(C ₅ H ₄ HgSeCN) ₂ TiCl ₄]	2140(s)	710(s), 720(s)	420(s), 425(s)
4.	[Fe(C ₅ H ₄ HgSeCN) ₂ ZrCl ₄]	2155(s)	760(s), 720(s), 780(s)	465(s), 418(m)
5.	[Fe(C ₅ H ₄ HgSeCN) ₂ HfCl ₄]	2160(s)	720(s), 750(w), 740(m)	480(s), 425(w)

s=strong; m= medium, w= weak and sh=shoulder

Conclusion

It can be concluded that ferrocenyl complexes display pharmacological and medicinal activities as antimicrobial agents against different microbes. The ferrocenyl complexes are more active than the free ligand and this activity depends on the metal ion and the tested microbes. For that, ferrocenyl complexes have attracted increasing attention of the scientists for searching of new potent pharmacological and medicinal activities.

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