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Studies on the complexes of Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV) chlorides with 1, 1 □ Bis (Thiocyanato mercurio) ferrocene.

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Abstract
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. In this paper I present study on a new series of complexes prepared from ferrocene derivatives with tetrachlorides of Si, Sn, Ti, Zr & Hf.

Keywords: Si(IV), Sn(IV), Ti(IV), Zr(IV), Hf(IV)

All the solvents used were of reagent grade and were purified and dried before use. Metal tetrachlorides, MCl_4 where M=Sn(IV), Si(IV), Ti(IV), Zr(IV), Hf(IV) and ferrocene were procured from BDH/Aldrich and used under strict dry conditions. All the reactions were carried out under dry nitrogen atmosphere.

Preparation of 1,1'bis-(thiocyanatomercurio)-ferrocene

Ferrocene (1.84g, 0.01mol) was dissolved in dry benzene (96ml) and to this was added a mathanolic solution of mercuric acetate in 1:1 molar ratio and stirred for 1h. to this reaction mixture, an aqueous solution of potassium thiocyanate was added in 1:1 molar ratio with continuous stirring. A yellow precipitate appeared which was filtered and washed with methanol. The residue was filtered and washed with methanol. The residue was refluxed with 1,2 dichlorethane in soxhlet apparatus to remove the soluble mono derivative and the bis derivative was filtered off, washed with benzene and pet. ether and recrystallized from DMSO.

Preparation of $[Fe(C_5H_4HgSCN)_2MCl_4]$ Where M=Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)

Tin tetrachloride (1.17ml, 0.01 mol) was dissolved in dried CCl_4 (100ml) and turbidity if any was removed by filtration. A homogeneous suspension of 1,1'-bis(thiocyanatomercurio)-ferrocene(7gm) in dried CCl_4 (100ml) separately prepared to this suspension, a solution of $SnCl_4$ was slowly added with constant strring and the clear solution was stirred for 48 hrs. A precipitate appeared which was filtered off, washed with CCl_4 and ether and dried in vacuo. Silicon & titanium derivatives were similarly prepared while Zirconium & hafnium were used suspensions. Yield about 65% .

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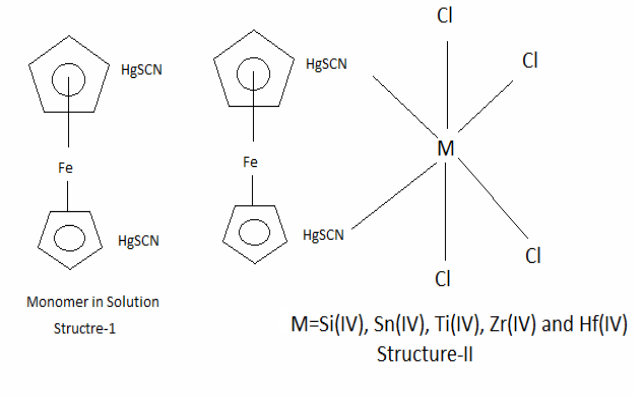
RESULT AND DISCUSSIONS

The complexes are non conducting in nature in DMSO. The IR spectra of 1,1'-bis(thiocynatomercurio))-ferrocene was recorded both in solid and solution phase. the solid phase spectra show the presence of three bands at 2190, 2120 and 2100 cm^{-1} which may be attributed to νC-N, two bands at 730, 720 cm^{-1} assigned to ν(C-S) and two bands 460, 410 cm^{-1} are due to δ(NCS) regions. In solution phase, only two bands at 2120 and 2100 cm^{-1} are observed while third band at 2190 cm^{-1}disappears.This shows that 1,1'-bis (thiocynatomercurio)-ferrocene is a dimer in solid while monomer in solution (structure -1).

On reaction with MCl_4 it forms adducts of the type $[Fe(C_5H_4HgSCN)_2MCl_4]$ the complexes are referred to as tetrachloro derivatives. The IR spectra of the tetrachloro complexes show the presence of ν(C-N) band in the region 2145-2165 cm^{-1}. Which is in the range of bridging thiocyanate group. The N-end of thiocyanate group of the ligand has co-ordinated with M of MCl_4 and has formed a thiocynate bridge (structure-II). The position of the band due to ν(C-S) and δ(NCS) also support the presence of a bridging thiocynate.

The log K value of the complexes have been experimently determined and result are presented in the table. The value suggest following order of stability of M-L band Zr<Hf<Ti<Si<Sn



Monomer in Solution
Structre-1

M=Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)
Structure-II

Sr.No.	Complex/Colour	mp^{0}C	Yield %	Found %						Log K
				S	N	Cl	Hg	M	Λ_m (in DMSO) $cm^2 mol^{-1}$	
1	$[Fe(C_5H_4HgSCN)_2SiCl_4]$/Dark Green	110	62	9.98	3.42	16.2	45.8	-	32.13	3.98
2	$[Fe(C_5H_4HgSCN)_2SnCl_4]$/Steel Gray	310	66	6.32	2.88	14.62	41.2	11.29	33.90	4.16
3	$[Fe(C_5H_4HgSCN)_2TiCl_4]$/Steel Gray	78	64	7.12	2.92	14.58	43.9	4.62	26.26	3.92
4	$[Fe(C_5H_4HgSCN)_2ZrCl_4]$/Dirty Green	296	60	6.78	2.94	14.98	41.89	9.60	32.75	2.82
5	$[Fe(C_5H_4HgSCN)_2HfCl_4]$/Dark Green	346	65	6.82	2.64	13.78	38.86	16.82	22.86	2.35

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