



^{119}Sn MÖSSBAUER SPECTROSCOPIC STUDIES OF TRIMETHYL TIN SUBSTITUTED IRON COMPOUND

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ABSTRACT:

The structural diagnosis and lattice dynamic of complexes $(\text{Me}_3\text{Sn})_3[\text{Fe}(\text{CN})_5\text{L}]_n \cdot x\text{H}_2\text{O}$ where L= 2-, 3- and 4- cyanopyridine, isonicotinamide and Nicotinic acid undertaken by means of ^{119}Sn Mössbauer spectroscopic techniques. The Mössbauer parameters of the complexes indicate that all the tin atoms are coordinated with three alkyl group and two cyano groups having trigonal bipyramidal structure. The asymmetry of the quadrupole splitting peak intensity observed in the ^{119}Sn Mossbauer spectra for the complexes was attributed to anisotropic mean square vibrational amplitude with respect to a molecular symmetry axis. Solid-solid phase transitions were clearly found in all the complexes at room temperature. The values of isomer shift (IS) and quadrupole splitting (QS) and the temperature dependence QS indicate that the tin atom in these complexes is in +4 oxidation state.

Keyword: ^{119}Sn Mössbauer spectroscopy, pentacyanoferrate(II)

INTRODUCTION:

Various kinds of trialkyl and triaryl tin complexes of transition metal cyanides by treating trialkyl and triaryl tin perchlorates with cyano compounds of transition metal have been synthesized^{1,2}. The crystal structure of $(\text{R}_3\text{Sn})_3[\text{M}(\text{CN})_6]_x$ determined using a single crystal x-ray diffraction method² consist of distorted octahedral $\text{Co}(\text{CNSn})_6$ fragments and a trigonal bipyramidal N_2SnMe unit within three dimensional network. The lattice displays strictly parallel channel. On the basis of IR spectra of those complexes Uson et al proposed that in every case the tin atoms are five coordinated with three alkyl or aryl groups in the equatorial position and two cyano groups in the axial position of trigonal bipyramidal and that tin and transition metal are bridged





by a cyano group. Katada et al^{3,4} have emphasized structural diagnosis and lattice dynamics of the coordination polymers $(\text{Me}_3\text{Sn})_3[\text{M}(\text{CN})_6]_x$ and trialkyl and triaryl tin complexes of transition metal cyanides by means of ^{119}Sn , and ^{57}Fe Mössbauer spectroscopy. U Behrens⁵ and coworkers have been synthesized complexes of the type $(\text{Me}_3\text{E}^{\text{IV}})_3[\text{M}^{\text{III}}(\text{CN})_6]_\infty$ ($\text{E} = \text{Pb}$ or Sn , $\text{M} = \text{Co}$ or Fe). Some cyanide-bridged 3D complexes derived from $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Fe}$, Cr , Mn) have been to display high $-T_c$, magneto-optical, gas storage and electrochemical properties⁶.

Mössbauer spectroscopy can provides valuable information about the nature chemical bonding and structure of compounds containing “Mössbauer” active atoms such a tin, iron and gold because Mössbauer parameters are sensitive to the number and nature of ligands coordinated to the Mössbauer atoms⁷⁻⁹. Earlier we have studied several alkyl and aryl substituted pentacyanoferrate (II) complexes¹¹⁻¹⁵. In the present work, ^{119}Sn Mössbauer spectroscopic work we have studies have been undertaken to examine the coordination of tin atoms and the lattice dynamical properties of tin sites in the title complexes.

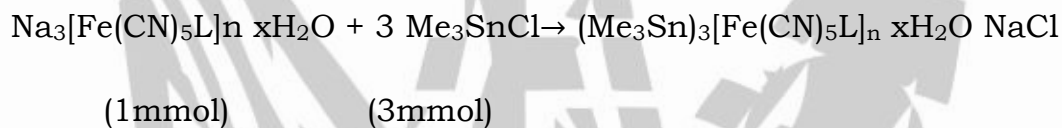
Experiment:

All reagents used were of AR, GR or high purity grade. The complexes were prepared by modifying the procedure.

Preparation of organotin substituted pentacyanoferrate(II) complexes

The stoichiometric amount of substituted pentacyanoferrate(II) (1mmol) and Me_3SnCl (3mmol) was undertaken in 20 mL ice cold water. The precipitated was obtained by adding ethanol dropwise. The precipitates were filtered off and washed with ethanol. The purity of the complexes was confirmed by elemental analysis for Fe, C, H and N.





Physical measurements

The Mössbauer effect measurements for ^{119}Sn were carried out by using constant acceleration type spectrometer. The isomer shift of ^{119}Sn spectra were reported with respect to BaSnO_3 respectively. The spectra were fitted with Lorentzian line shapes by using least square fitting procedure. UV-visible spectra of the organotin heterocyclic substituted pentacyanoferrate(II) complexes were recorded in aqueous solution using Hitachi Model U-3500 spectrophotometer and 1cm path length. Infrared spectra were obtained on a sample in KBr pallets using Hitachi Nicolet Model_I 5040 FTIR spectrophotometer. The thermogravimetric (TGA-DTA) were carried out using Seiko Instrument Inc.SSC/5200. The DSC Curve were recorded between 273K and 785K on RIGAKU Thermoflex Apparatus at scanning rate 5Kmin^{-1} .

RESULT AND DISCUSSION:

All the complexes were coloured solid and stable under normal atmospheric conditions. Analytical data, electronic spectral bands and characteristic IR frequencies due to $\nu(\text{CN})$, $\delta(\text{Fe-CN})$, $\nu(\text{Fe-C})$, $\nu(\text{Sn-C})$ and $\nu(\Delta\text{C}\equiv\text{N})$ are listed in Table 1. ^{119}Sn Mössbauer spectra of all the complexes obtained at 298K are shown in Fig.1 while the Mössbauer parameters such as isomer shift(IS), quadrupole splitting (QS) and halfwidth (Γ_{exp}) derived from the observed spectra are summarized in Table 1. The spectra consist of one doublet with small quadrupole splitting QS may be seen the same Fig.1. The values of IS and QS indicate that the tin atom in this complexes is at +4 state. The DTA, DTG and DSC of organotin pyrrole substituted complex are shown in Fig.2.



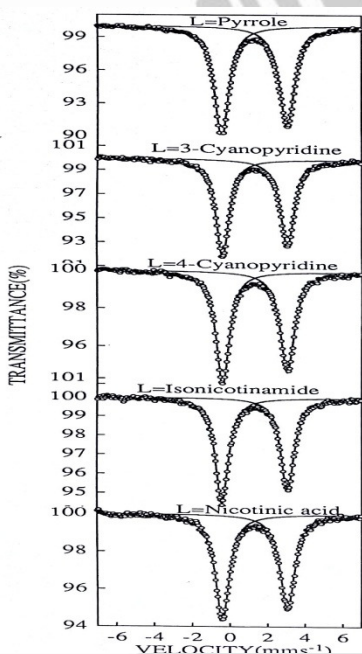


Fig. 1. ^{119}Sn Mossbauer spectra of trimethyl tin substituted pentacyanoferrate (II) complexes.

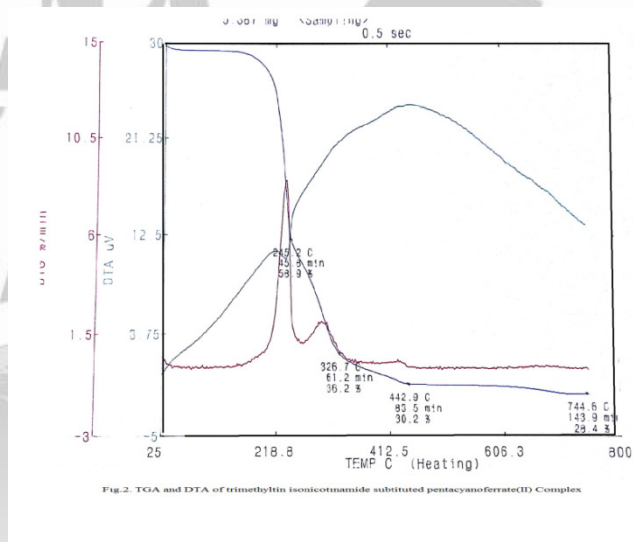


Fig. 2. TGA and DTA of trimethyl tin substituted pentacyanoferrate (II) complexes.

When one of the cyano ligands in $[\text{Fe}(\text{CN})_6]^{4-}$ is replaced by neutral heterocyclic ligand L to give $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$, the octahedral geometry remain affected but symmetry is lowered from O_h to approximately C_{4v} . Even though the electronic configuration will be t_{2g}^6 , it will further split into d_{yz} , d_{zx} , d_{xy} (also called e and b_2)^{10,14}. All complexes are expected to be diamagnetism. The heterocyclic bases coordinating through N-atom are essentially σ -donors¹⁰⁻¹⁵. On the other hand, five CN^- ligands have vacant Π_{2py}^* , $2p_z^*$ orbital available for backbonding.



Table 1: ^{119}Sn Mossbauer parameter of $(\text{Me}_3\text{Sn})_3[\text{Fe}(\text{CN})_5\text{L}]$ complexes at room temperatures

Sr. No.	Complex $(\text{Me}_3\text{Sn})_3[\text{Fe}(\text{CN})_5\text{L}]$ L=	Temp (K)	(δ) mms^{-1}	(ΔE_Q) , mms^{-1}	Γ_{exp} mms^{-1}
^{119}Sn					
1	2-cyanopyridine	273	1.32	3.45	0.83, 0.87
2	3-cyanopyridine	273	1.33	3.44	0.85, 0.91
3	4-cyanopyridine	273	1.31	3.44	0.84, 0.90
4	Isonicotinamide	273	1.31	3.47	0.84, 0.86
5	Nicotinic acid	273	1.33	3.45	0.88, 0.92

Table 2: Infrared Spectral data of $(\text{Me}_3\text{Sn})_3[\text{Fe}(\text{CN})_5\text{L}]$ complexes at room temperatures

Sr. No	Complex $(\text{Me}_3\text{Sn})_3[\text{Fe}(\text{CN})_5\text{L}]$ L=	$\nu(\text{CN})$	$\delta(\text{Fe-CN})$	$\nu(\text{Fe-C})$	$\Delta\nu(\text{CN})$	$\nu(\text{Sn-C})$
1	2-cyanopyridine	2075s 2140vw	552s	420m	65	580vw
2	3-cyanopyridine	2072s 2122w	552s	451m	50	582s
3	4-cyanopyridine	2072s 2145w	552s	455m	73	580s
4	Isonicotinamide	2075s 2125w	552w	451w	50	580w
5	Nicotinic acid	2072s 2125w	552s	445w	53	582w





Aqueous solution of pentacyanoferrate (II) exhibiting an absorption in the UV-visible region. In d^6 pentacyanoferrate(II) of C_{4v} symmetry for which the ground state is 1A_1 and low energy excited states of the same multiplicity are 1A_2 and $^1E_{(1)}$ ¹⁴. Thus two $d-d$ transitions are typically observed for such complexes $^1E_{(1)} \leftarrow ^1A_1$ and $^1A_2 \leftarrow ^1A_1$. The first band with energy and intensity considerably greater than second has been assigned to $^1E_{(1)} \leftarrow ^1A_1$ transition. The second, a weak band occurred at lower energies and should be relatively insensitive to the ligand L. The $^1A_2 \leftarrow ^1A_1$ is expected at 310nm (31kK) but it is not observed for the pentacyanoferrate(II) complexes in the region 264-444 nm¹⁴. By analogy, considering their energy and intensity, the band due to $^1E_{(1)} \leftarrow ^1A_1$ in pentacyanoferrate(II) is found in the region 387-404nm. As the $d-d$ bands have large and asymmetric form, we suggest that $^1A_2 \leftarrow ^1A_1$ transitions occur superimposed on the $^1E_{(1)} \leftarrow ^1A_1$ in the spectra of the studied complexes. (Expressions relating isomer shifts in Mössbauer spectra with the electronic structure of tin in its compounds are obtained. These expressions give a description of isomer shifts for chemical compounds of different types: tetravalent tin when there is π bonding (tin tetrahalogenides), tetravalent tin in the absence of π bonding (compounds where tin is bound with alkyl, aryl, and carbonyl metal radicals), bivalent tin, etc. The expressions obtained were used for analysis of the electronic structure of tin in compounds of these classes. For tetravalent tin compounds with π bonding the change of isomer shift δ towards negative values (with respect to α -Sn) is found to be accounted for by a decrease, and for compounds without π bonds by an increase in the number of valence 5s electrons (S) at $S > 1$.)





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