MÖSSBAUER SPECTROSCOPIC STUDIES OF BIS(TRI-n-BUTYLTIN) SULFATE, SELENATE, AND CHROMATE

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The Mössbauer parameters of bis(tri-n-butyltin) sulfate, selenate, and chromate have been determined in order to elucidate the intermolecular inter-action of such species in solid state. The absolute values of recoilfree fraction have been estimated in the temperature range from 80 to 200 K and the mean square displacement of tin atom has been determined. From the results, as well as from the temperature dependence of quadrupole split line asymmetry, non-polymeric structure is inferred for those three compounds.

Since the Mössbauer spectroscopic studies of several trialkyltin sulfate analogues have been done, controversy has arisen over the structure of the com-pounds. Ford et al. have reported that trimethyltin sulfate, selenate, and chromate possess polymeric structures involving five or six coordinate tin in the solid state.[1,2] On the other hand, Stapfer et al. have reported that bis(tri-n-butyltin) sulfate has a non-polymeric (monomeric binuclear) structure in the solid state.[3,4]

The discrepancy seems to be due to some ambiguities in the interpretation of IR and Mössbauer data. In their studies,[1-3] the argument for polymer or non-polymer structure rests mainly upon the success or failure to observe Mössbauer absorption with the absorber at room temperature and no data are available con-cerning with thickness of the absorbers. Although the temperature dependence of the resonance effect magnitude has been determined qualitatively for bis(tri-n-butyltin) sulfate, no absolute value of the recoilfree fraction (Lamb-Mössbauer factor) has been reported for these compounds.[4]

We have shown that the "polymer effect" enhances the absolute value of the recoilfree fraction in an absorber, f_a, by restricting the motion of the mole-cule in the direction of the polymer bonding and reduces its temperature depen-dence, df_a/dT, even in the non-Debye solids,[5-11] except for in the case of helical chain polymers.[12,13] We have also proposed that a negligible asymmetry of quadrupole split lines is observed in the case of non-polymer or three-dimen-sional polymer compounds.[6] This proposal has so far been proved for a number
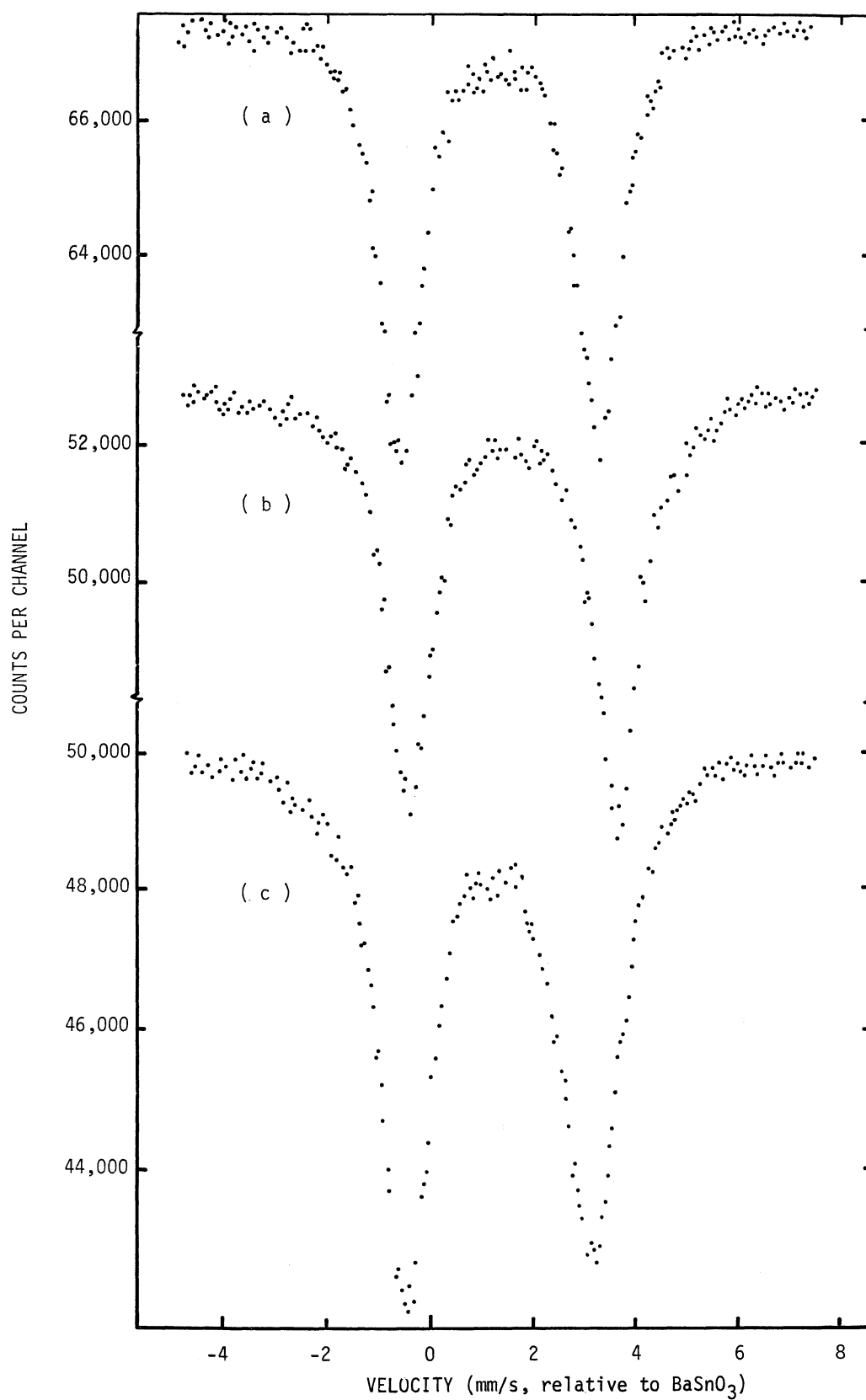
Fig. 1. The Mössbauer spectra of (a) bis(tri-n-butyltin) sulfate, (b) bis(tri-n-butyltin) selenate, and (c) bis(tri-n-butyltin) chromate at 80 K.
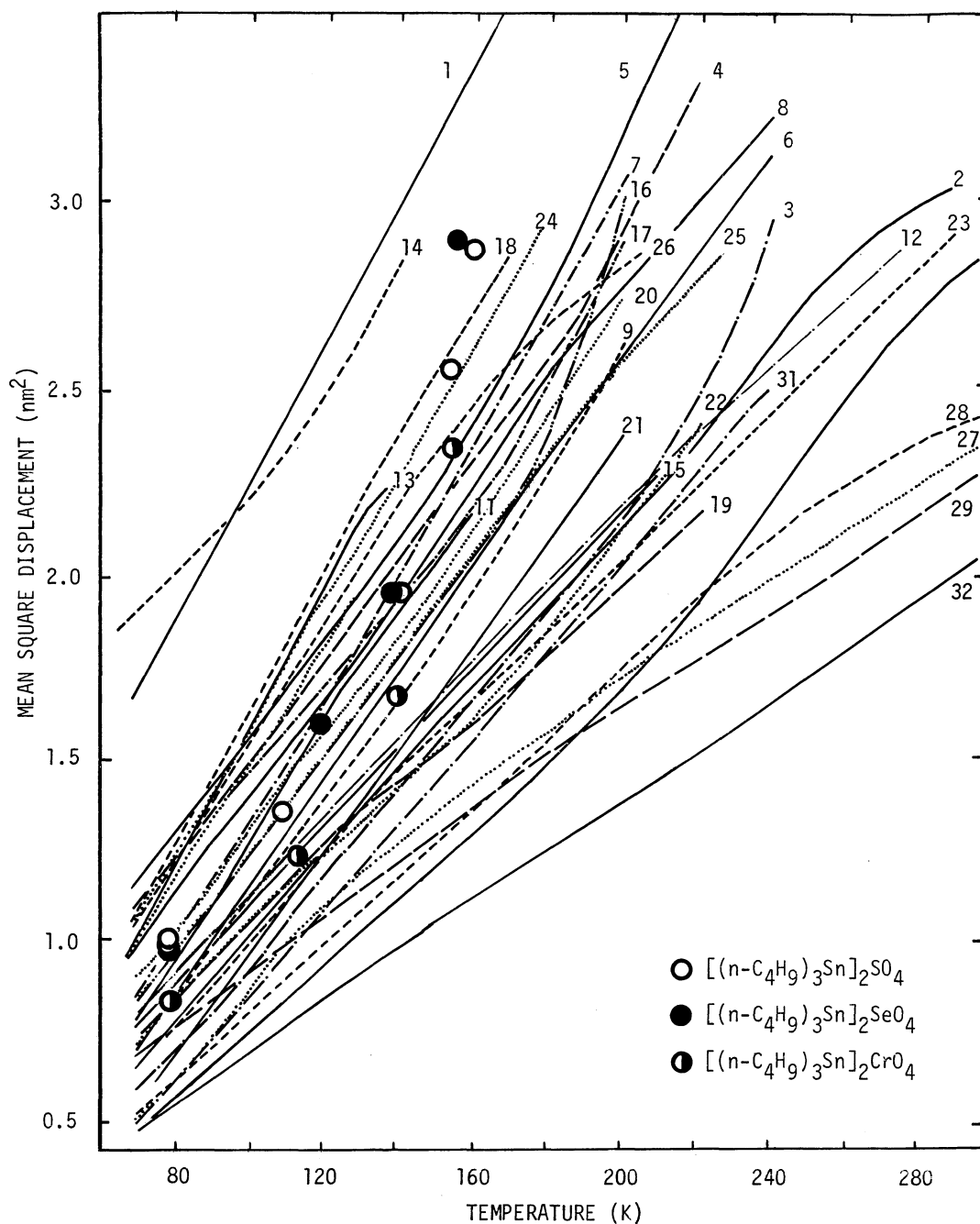
Fig. 2. The temperature dependence of the mean square displacement for the organotin compounds.
1. Me_4Sn,[5] 2. Ph_4Sn,[5] 3. $(C_6H_{11})_4Sn$,[24] 4. Ph_3SnH,[5] 5. Ph_2SnH_2,[5] 6. Ph_6Sn_2,[5] 7. $(Ph_3Sn)_4Sn$,[5]
8. $(Ph_2Sn)_6$,[24] 9. $Ph_3Sn(C_6F_5)$,[23] 10. $Ph_2Sn(C_6F_5)_2$,[23] 11. $(C_6F_5)_4Sn$,[23] 12. $(Me_3SnF)_n$,[12] 13.
Me_3SnCl,[10] 14. Me_3SnBr,[10] 15. Me_2SnBr_2,[10] 16. $(Me_3SnOH)_n$,[6] 17. $(Me_3SnCN)_n$,[6] 18. $Me_3SnClPy$,[5] 19.
Me_2SnCl_2Bipy,[5] 20. $(Me_3SnOCOH)_n$, $(Ph_3SnOCOCH_3)_n$, $[Ph_3SnOCO(CH_2)_2COCH_3]_n$,[12] 21. $Ph_3SnOCO(CH_3)CH_2$,[13]
22. $Me_2SnAcac_2$,[24] 23. $(Ph_3SnF)_n$,[12] 24. Ph_3SnCl,[5] 25. Ph_2SnCl_2,[5] 26. $PhSnCl_3$,[10] 27. $(Me_2SnO)_n$,[24]
28. $(Ph_2SnO)_n$,[8] 29. $[Me_2Sn(OCOH)_2]_n$,[5] 30. $(Oct_2SnO)_n$,[10] 31. $[Ph_2SnO(C_6H_4)]_n$,[8] 32. $(SnTdt_2)_n$.[5]
Me: methyl; Ph: phenyl; Oct: octyl; Py: pyridine; Bipy: bipyridyl; Acac: acetylacetonate; Tdt: tol-
uene-3,4-dithiolate. Compounds no. 12, 16, 17, 20, and 23 are known as one-dimensional polymers
and compounds no. 27, 28, 29, 30, 31, and 32 are known as two- or three-dimensional polymers in
solid.

of compounds.[6-10,20]   In order to clarify whether bis(tri-n-butyltin) sulfate, selenate, and chromate have a polymer structure or not, we have investigated the absolute values of recoilfree fraction and the line asymmetry of these compounds in the temperature range from 80 to 200 K.

The compounds used in the present studies were synthesized from tri-n-butyl-tin chloride and silver sulfate, selenate, and chromate respectively, by following the methods described in Refs. 1 and 10.   The purity of samples was checked by elemental analyses: Anal. Found: H, 8.04; C, 42.53.   Calcd. for $[(C_4H_9)_3Sn]_2$-SO_4: H, 8.05; C, 42.63%.   Found: H, 7.64; C, 41.30.   Calcd. for $[(C_4H_9)_3Sn]_2SeO_4$: H, 7.44; C, 39.87%.   Found: H, 7.52; C, 40.06.   Calcd. for $[(C_4H_9)_3Sn]_2CrO_4$: H, 7.82; C, 41.41%.

The ^{119}Sn-Mössbauer spectra were measured against a barium stannate source moving in a constant acceleration mode at room temperature.   The sample was used as an absorber and kept in a cryostat.   Slushy ether was used as a constant temperature coolant instead of a liquid nitrogen-heater system in order to avoid the line broadening due to bubbling at temperatures above 140 K.[15]   The experimental details pertaining to the Mössbauer spectrometer, the barium stannate source and absorber, the velocity calibrations, and the behavior of the resonance absorption area associated with a Mössbauer resonance line with respect to the line width and the line intensity have already been described elsewhere.[10,15-17]   The compounds were obtained in fine polycrystalline powders, i. e., the absorbers were randomly oriented crystallites.   The recoilfree fraction was evaluated according to the methods reported in Refs. 10 and 18.

Typical Mössbauer spectra of the compounds are shown in Fig. 1 and the

Table 1.   Mössbauer parameters at 80 K for compounds which are discussed in text.

Compound	Isomer shift (mm/s; relative to BaSnO$_3$)	Quadrupole splitting (mm/s)	Recoilfree fraction	Reference
$[(n-C_4H_9)_3Sn]_2SO_4$	1.54 ± 0.03	3.87 ± 0.03	0.240 ± 0.005	This work
$[(n-C_4H_9)_3Sn]_2SO_4$	1.56 ± 0.02	4.01 ± 0.02	---	4
$[(CH_3)_3Sn]_2SO_4$	1.37 ± 0.05	4.06 ± 0.05	---	1
$[(n-C_4H_9)_3Sn]_2SeO_4$	1.69 ± 0.03	4.09 ± 0.03	0.246 ± 0.005	This work
$[(CH_3)_3Sn]_2SeO_4$	1.39 ± 0.05	4.09 ± 0.05	---	1
$[(n-C_4H_9)_3Sn]_2CrO_4$	1.58 ± 0.03	3.71 ± 0.03	0.302 ± 0.005	This work
$[(CH_3)_3Sn]_2CrO_4$	1.36 ± 0.05	3.77 ± 0.05	---	1

Mössbauer parameters extracted from the spectra are summarized in Table 1. The
values of isomer shift and quadrupole splitting are in good agreement with re-
lated data reported for bis(tri-n-butyltin) sulfate and bis(trimethyltin) sul-
fate, selenate, and chromate, respectively. Slightly larger values of isomer
shift are found for tri-n-butyltin compounds compared to those for the correspond-
ing trimethyltin compounds, as generally observed for a series of alkyltin com-
pounds.[21,22] The mean square displacement, $<u^2>$, was evaluated from the recoil-
free fraction, f_a, by using the following relation,

$$f_a = \exp[-4\pi^2 <u^2>/\lambda^2],$$

where λ is the wave length of Mössbauer γ-ray.

The temperature dependence of the spatially averaged mean square displacement
is shown in Fig. 2. Our data obtained earlier are also illustrated in Fig. 2 for
tha sake of comparison. It was demonstrated that the spatially averaged mean
square displacement is strongly dependent upon the nature of the polymeric struc-
ture which directly involves the bonding of the Mössbauer atom[5,6,10,11] and that
the mean square displacement is smallest along the chain axis for the linear-chain
(or one-dimensional) polymers and is also smallest in the plane of the layer for
the layer-type (or two-dimensional) polymers.[6-10]

As seen in Fig. 2, the mean square displacement data obtained for bis(tri-n-
butyltin) sulfate, selenate, and chromate are all found in the region of either
non-polymeric compounds or one-dimensional polymer compounds. The trends of tem-
perature dependence of the mean square displacement or the recoilfree fraction for
these compounds agree with that of temperature dependence of spectral area report-
ed by Herber for bis(tri-n-butyltin) sulfate,[4] although a precise comparison can
not be made since the absolute values of recoilfree fraction have not been esti-
mated in Ref. 4. The results indicate that the three- and two-dimensional poly-
mer structures can be ruled out for these compounds. Anomalously enhanced mean
square displacement values observed for all these compounds above ca. 150 K sug-
gest that some kind of intramolecular vibrational or librational mode may begin
to contribute to the mean square displacement of tin atoms at the high tempera-
ture. A similar trend is found for tetracyclohexyltin, in which the increased
mean square displacement at high temperature region may be ascribed to the con-
formational vibration of cyclohexyl rings.

No significant temperature-dependent quadrupole line asymmetry, expressed as
the ratio of the area under the positive velocity component to the area under the
negative component of the quadrupole split doublet, is found in any of these com-
pounds. Since this asymmetry arises from the angular dependence of the vibra-
tional amplitude of the Mössbauer atom,[19] especially due to anisotropy of inter-
molecular interaction in molecular solids,[6-10] the results suggest that the com-
pounds have neither one-dimensional nor two-dimensional polymer structure but
either non-polymer (low molecular weight species) or three-dimensional polymer
structure.

On the basis of the results obtained from the temperature dependence of the
recoilfree fraction as well as from the absence of a temperature dependent quad-
rupole split line asymmetry, it may be concluded that all the compounds investi-

gated here, bis(tri-n-butyltin) sulfate, selenate, and chromate, possess non-polymeric structures, in consonance with the result reported for bis(tri-n-butyltin) sulfate[3,4] but in disagreement with those for bis(trimethyltin) sulfate, selenate, and chromate.[1,2]

REFERENCES

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1) B. F. E. Ford, J. R. Sams, R. G. Goel, and D. R. Ridley, *J. Inorg. Nucl. Chem.*, 33, 23 (1971); Paper T7 presented at the IVth International Conference on Organometallic Chemistry, Bristol, England, July 28 - Aug. 1, 1969.

2) R. E. B. Garrod, R. H. Platt, and J. R. Sams, *Inorg. Chem.*, 10, 424 (1971).

3) C. H. Stapfer, K. L. Leung, and R. H. Herber, *Inorg. Chem.*, 9, 970 (1970).

4) R. H. Herber, *J. Chem. Phys.*, 54, 3755 (1971).

5) H. A. Stöckler, H. Sano, and R. H. Herber, *J. Chem. Phys.*, 47, 1567 (1967).

6) H. A. Stöckler and H. Sano, *Phys. Letters*, 25A, 550 (1967).

7) H. A. Stöckler and H. Sano, *Phys. Rev.*, 165, 406 (1968).

8) H. A. Stöckler and H. Sano, *Polymer Letters*, 7, 67 (1969).

9) H. A. Stöckler and H. Sano, *Chem. Commun.*, 1969, 954.

10) H. A. Stöckler and H. Sano, *J. Chem. Phys.*, 50, 3813 (1969).

11) H. Sano, M. Aratani, and H. A. Stöckler, *Phys. Letters*, 26A, 559 (1968).

12) H. A. Stöckler and H. Sano, *Chem. Phys. Letters*, 2, 448 (1968).

13) H. Sano and R. Kuroda, *Chem. Phys. Letters*, 11, 512 (1971).

14) H. C. Clark and R. G. Goel, *Inorg. Chem.*, 4, 1428 (1965).

15) H. A. Stöckler and H. Sano, *Nucl. Instr. Methods*, 44, 103 (1966).

16) H. Sano and R. H. Herber, *J. Inorg. Nucl. Chem.*, 30, 409 (1968).

17) H. Sano, "Mössbauer Spectroscopy. The Chemical Applications", Kodansha, Tokyo, 1972.

18) G. Lang, *Nucl. Instr. Methods*, 24, 425 (1963).

19) S. V. Karyagin, *Dokl. Akad. Nauk. (SSSR)*, 148, 1102 (1963); English translation: *Proc. Acad. Sci. (USSR), Phys. Chem. Sect.*, 148, 110 (1963).

20) R. H. Herber and S. C. Chandra, *J. Chem. Phys.*, 52, 6045 (1970); 53, 3330 (1970); 54, 1847 (1971).

21) S. Onaka and H. Sano, *Bull. Chem. Soc. Japan*, 48, No. 1 (1975).

22) J. J. Zuckerman, "Advances in Organometallic Chemistry," Vol. 9, p. 21, Academic Press, New York, N. Y., 1970.

23) H. A. Stöckler and H. Sano, *Trans. Faraday Soc.*, 64, 577 (1968).

24) Unpublished data.