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Abstract

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FEATURES OF THE MÖSSBAUER EFFECT FOR TIN COMPOUNDS WITH COORDINATION NUMBER SIX

The chemical shift and quadrupole splitting of Mössbauer spectral lines—characteristics directly dependent on the structure of the electron shells of the emitters and absorbers of gamma quanta—make it possible, as is well known, to isolate and quantitatively investigate the role of both the bonds nearest to the Mössbauer atoms and more distant chemical bonds (^1). It is precisely these characteristics that have so far served as the main basis of the new method of chemical physics now being created—Mössbauer molecular spectroscopy. Thus, for example, the difference in the magnitudes of the chemical shifts (δ) and quadrupole splittings (Δ) of the lines of Mössbauer spectra has made it possible not only to carry out a clear qualitative distinction between compounds of divalent and tetravalent tin, but also to establish quantitative differences in the nature of the bonds in various compounds of both of these types, and also to note the specificity of such organotin compounds in which tin has coordination number five (^2, ^3).

In the present work new possibilities for using the Mössbauer effect in chemistry are shown; namely, it is demonstrated that the probability itself of recoil-free resonant gamma fluorescence (the Debye-Waller factor), as well as the character of its temperature dependence, depend in an essential way on the structure of compounds of Mössbauer atoms.

It is shown that the principal distinguishing features of the Mössbauer effect in tin compounds with coordination number six are a very high probability of recoil-free resonant gamma fluorescence at low temperatures (78° K) and the preservation of a quite appreciable effect at room temperature. It is precisely these features, and not the magnitudes of the chemical shifts or quadrupole splittings, that can serve as the most reliable basis for identifying all possible tin compounds with coordination number six. It is precisely the appearance or disappearance of the Mössbauer effect at room temperature that can provide the best method for observing the kinetics of various transformations involving the appearance or decomposition of such tin compounds. A quantitative interpretation of the results obtained must be given subsequently, as new experimental data accumulate. Their qualitative interpretation, however, is quite obvious. The large total strength of the six bonds of tin atoms formed in different types of octahedral structures (O_h, D_{4h}, or D_{2h}), owing to the corresponding variants of sp^3d^2 hybridization, ensures the smallness of the mean-square displacements $\overline{\chi^2}$ of Sn atoms in the lattice in comparison with the square of the wavelength of the resonance quanta λ^2, and, accordingly, large Debye-Waller factors (⁀4),

$$f' = \exp\left\{-\frac{\overline{\chi^2}}{\lambda^2}\right\}.$$

Furthermore, compounds of Sn with coordination number six are characterized by lattices with an especially large number (N) of atoms in the unit cell, and consequently also by the greatest number of optical branches ($3N - 3$) in the vibrational spectrum. Meanwhile, it is precisely the large contribution of the optical branches that determines the anomalously weak temperature dependence of the probability of the Mössbauer effect (⁀5).

The list of compounds investigated by us and the chemical shifts obtained for them (relative to β-Sn) is given in Table 1; Table 2 gives the probabilities of the Mössbauer effect in relative units. Most of the compounds studied belong to complexes of the type $\mathrm{SnHal_4 \cdot nAm}$, where $\mathrm{Hal} = \mathrm{Cl, Br, J}$; $n = 2, 3, 4$; Am denotes the organic molecules listed in the footnote to Table 1.

The tin halide derivatives $SnCl_4$, $SnBr_4$, SnJ_4 are tetrahedral structures, in which the Sn atoms give four valence bonds through sp^3 hybridization. In these compounds the Debye-Waller factor at 78°K is considerably smaller than in the complex, and at room temperature the Mössbauer effect is not observed at all. Filling of the valence $5d$ orbitals of tin in the complexes $\mathrm{SnHal_4 \cdot nAm}$ with a coordination number of Sn equal to six leads, as a rule, to a decrease in the values of $|\psi(0)|^2$ in comparison with those characteristic of the four sp^3 bonds in the initial compounds $\mathrm{SnHal_4}$. An analogous decrease of $|\psi(0)|^2$ with increasing number of $3d$ electrons, owing to shielding of the s electrons of the inner shells of iron atoms, is known from calculations [6] and was taken in [7] as the basis for interpreting the chemical shifts of the lines of the Mössbauer spectra of iron compounds. In the case considered, the shielding action of the $5d$ electrons has an especially strong effect on the outer $5s$ electrons. Accordingly, the decrease in $|\psi(0)|^2$, i.e., as it were, an effective increase in the degree of ionicity of the Sn –Hal bond upon going to the complexes, is manifested the more strongly, the more covalent were the bonds in the initial compound $\mathrm{SnHal_4}$–strongest of all in SnJ_4, then in $SnBr_4$, and finally in $SnCl_4$. As a result, the magnitude of the chemical shift in the octahedral D_{4h} complexes $\mathrm{SnHal_4 \cdot nAm}$, where the four Hal atoms lie in one plane XOY (sp^2d hybridization), and the organic molecules are attached along the Z axis ($p_{zd_z^2}$ hybridization), which is a fourth-

Fig. 1. Change in the chemical shift ($-\delta$, mm/sec) in the complexes $\mathrm{SnHal_4 \cdot nEn}$. ($\mathrm{Hal = Cl, Br, J}$; $n = 0, 2, 3, 4$); a—$\mathrm{SnCl_4}$, b—$\mathrm{SnBr_4}$, c—$\mathrm{SnJ_4}$.

Figure 1: Fig. 1. Change in the chemical shift ($-\delta$, mm/sec) in the complexes $\mathrm{SnHal_4 \cdot nEn}$. ($\mathrm{Hal = Cl, Br, J}$; $n = 0, 2, 3, 4$); a—$\mathrm{SnCl_4}$, b—$\mathrm{SnBr_4}$, c—$\mathrm{SnJ_4}$.

order symmetry axis, already depends little on the nature of the halogen; and in the case of complexes with diamines it increases only weakly on going from ethylenediamine to hexamethylenediamine, and also with an increase in the number of diamine molecules bound to $\mathrm{SnHal_4}$, as is seen from Fig. 1. The possibility of attaching to a complex with two diamine molecules one or two additional similar molecules can be explained as follows [8]. When diamines are added to $\mathrm{SnHal_4}$, electrons are transferred from the nitrogen atoms of amino groups adjacent to tin to the 5d shells of the tin atoms. Therefore the N—H bond is weakened, and the hydrogen atom passes to the second amino group.

Fig. 1. Change in the chemical shift ($-\delta$, mm/sec) in the complexes $\mathrm{SnHal_4 \cdot nEn}$. ($\mathrm{Hal = Cl, Br, J}$; $n = 0, 2, 3, 4$); a—$\mathrm{SnCl_4}$, b—$\mathrm{SnBr_4}$, c—$\mathrm{SnJ_4}$.

$$\begin{aligned} \mathrm{Hal_4Sn \cdots NH_2(CH_2)_{nNH}2} &\longrightarrow \mathrm{Hal_4Sn \cdots \bar{N}H(CH_2)_{nNH}3^+} \\ \mathrm{\cdots NH_2(CH_2)_{nNH}2} &\longrightarrow \mathrm{\cdots \bar{N}H(CH_2)_{nNH}3^+} \end{aligned}$$

As a result, the compounds $\mathrm{SnHal_4 \cdot 2Am}$ are dibasic complex acids capable of attaching bases—excess diamine molecules—through secondary acid-base interaction in the outer sphere of the complex. Such attachment, as is seen from the data of Table 1 and Fig. 1, already has very little effect on the magnitude of the chemical shift. The explanation given, which is also confirmed by the data

Table 1

Values of chemical shifts ($-\delta$) for the compounds studied*

No.	Compound**	$-\delta$, mm/s	No.	Compound**	$-\delta$, mm/s
1	$\mathrm{SnO_2}$	2.70	21	$\mathrm{SnBr_4}$	1.25
2	$\mathrm{SnCl_4}$	2.00	22	$\mathrm{SnBr_4 \cdot 2NH_4Cl}$	2.05
3	$\mathrm{SnCl_4 \cdot 2NH_4Cl}$	2.43	23	$\mathrm{SnBr_4 \cdot 2En}$	2.27
4	$\mathrm{[C_6H_5NH_3]_2SnCl_6}$	2.21	24	$\mathrm{SnBr_4 \cdot 3En}$	2.38
5	$\mathrm{SnCl_4 \cdot 5H_2O}$	2.37	25	$\mathrm{SnBr_4 \cdot 4En}$	2.70
6	$\mathrm{SnCl_4 \cdot 2NH_4J}$	2.16	26	$\mathrm{SnBr_4 \cdot 4Tmd}$	2.57

No.	Compound**	–δ, mm/s	No.	Compound**	–δ, mm/s
7	$SnCl_4 \cdot$ 2En	2.20	27	$SnBr_4 \cdot$ 2Hmd	2.48
8	$SnCl_4 \cdot$ 3En	2.48	28	$SnBr_4 \cdot$ 3Hmd	2.70
9	$SnCl_4 \cdot$ 4En	2.59	29	$SnBr_4 \cdot$ 4Hmd	2.70
10	$SnCl_4 \cdot$ 2Tmd	2.59	30	$SnBr_4 \cdot$ $2(CH_2–$ $CH_2–$ COOH)	2.15
11	$SnCl_4 \cdot$ 3Tmd	2.59	31	$SnBr_4 \cdot$ $2(NH_2)_2CS$	1.90
12	$SnCl_4 \cdot$ $2C_5H_5N$	2.70	32	SnJ_4	1.00
13	$SnCl_4 \cdot$ $2[CH_3–$ CH– COOH]	2.30 |	33	$SnJ_4 \cdot$ 2En NH_2	2.27
14	$SnCl_4 \cdot$ $2[(CH_3)_2(CH)_2NH_2COOH]$	2.70	34	$SnJ_4 \cdot$ 3En	2.58
15	$SnCl_4 \cdot$ $2C_5H_{11}N \cdot$ $2CH_3COOH$	2.70	35	$SnJ_4 \cdot$ 4En	2.70
16	$SnCl_4 \cdot$ $2(NH_2)_2CS$	1.75	36	SnF_4***	3.17
17	$SnCl_4 \cdot$ $2C_4H_8S$	1.89	37	K_2SnF_6	3.20
18	$SnCl_4 \cdot$ $2C_4H_8O$	2.00	38	Cs_2SnF_6	3.14
19	$SnCl_4 \cdot$ $C_5H_5N \cdot$ CH_3COOH	2.27	39	$(HC\ CCOO)_4Sn$	2.70
20	$SnCl_4 \cdot$ $C_5H_{11}N \cdot$ CH_3COOH	2.39	40	$ClSn(CH_2NO_2)_3$	2.70

* The values of the chemical shifts (–δ, mm/s) are given relative to the γ-transition in β-Sn. The value of –δ for SnO_2 was taken equal to 2.70 mm/s. The accuracy of the measurement is everywhere ±0.08 mm/s.

** Designations in the table: En–ethylenediamine $[NH_2(CH_2)_2NH_2]$; Tmd –tetramethylenediamine $[NH_2(CH_2)_4NH_2]$; Hmd–hexamethylenediamine $[NH_2(CH_2)_6NH_2]$; C_5H_5N–pyridine; $C_5H_{11}N$–piperidine; C_4H_8S–tetrahydrothiophene; C_4H_8O–tetrahydrofuran.

*** Of all the compounds studied, quadrupole splitting, equal to 1.66 mm/s, was found only for SnF_4.

Table 2

Values of af', in percent, for some of the compounds studied at $T = 78°$K and $T = 300°$K*

No.	Compound	af', % at $T = 78°$K	af', % at $T = 300°$K	No.	Compound	af', % at $T = 78°$K	af', % at $T = 300°$K
1	$SnCl_4$	0.6	0.0	10	$SnBr_4 \cdot 2En$	3.1	0.4
2	$SnCl_4$ $CH_3COOH \cdot C_5H_5N$	2.6	0.5	11	$SnBr_4 \cdot 3En$	2.5	0.7
3	$SnCl_4CH_3COOH$ $C_5H_{11}N$	2.7	0.5	12	$SnBr_4 \cdot 4Hmd$	2.6	0.5
4	$SnCl_4 \cdot 2Tmd$	4.2	1.1	13	SnF_4	6.2	4.5
5	$SnCl_4 \cdot 5H_2O$	2.2	0.2	14	K_2SnF_6	2.4	0.9
6	$[SnCl_6][C_6H_5NH_3]_2$	3.4	0.6	15	Cs_2SnF_6	2.3	1.0
7	$SnCl_4 \cdot 2NH_4Cl$	2.8	0.5	16	$(HC\ CCOO)_4Sn$	18.2	7.8
8	$SnCl_4 \cdot 2NH_4J$	3.5	0.5	17	$ClSn[CH_2NO_2]_3$	6.8	0.2
9	$SnBr_4$	0.6	0.0	18	SnO_2	3.8	2.8

* The accuracy in determining af' is everywhere ±0.1%.

IR spectra makes it possible to understand the impossibility of addition of two $SnHal_4$ molecules to diamines.

As is seen from a comparison of the data in Table 1, for $SnCl_4$ and $SnCl_6''$ the transition from four to six bonds of tin with a given atom (here, with Cl) has little effect on the magnitude of the chemical shift. The agreement of the chemical shift for SnO_2 (coordination number of Sn = 6 ([9])) with that expected, in accordance with the electronegativity of oxygen, in the series of compounds SnX_4 ([1,10]) also testifies to this. It will be of interest to check the magnitudes of the chemical shifts for the complexes $SnBr_6''$ and SnJ_6''. Thus, chemical shifts cannot

serve as a clear basis for choosing between two bonding variants: SnX_4 with sp^3-hybridization or SnX_6 with sp^3d^2-hybridization. The magnitude of the Debye–Waller factor and its temperature dependence make such a choice possible. Thus, for example, on the basis of the data in Tables 1 and 2 we are inclined to

Fig. 2. Proposed structure of SnF4

Figure 2: Fig. 2. Proposed structure of SnF4

assert that, even in such compounds as tin tetrapropiolate $(HC \equiv CCOO)_4Sn$ and trimethylnitrotin chloride $ClSn(CH_2NO_2)_3$, the tin atoms have coordination number six. Despite the fact that the chemical shifts for these two compounds are identical and equal to $\delta(SnO_2)$, one can immediately assert, without additional analyses, that in all three cases we studied different individual compounds, and not, say, an admixture of SnO_2, since different temperature dependences or different absolute values of the Mössbauer-effect probability were observed.

Fig. 2. Proposed structure of SnF_4

One of the curious circumstances requiring further special, detailed analysis is the absence, in the spectra of all the compounds listed in Table 1, of quadrupole splitting resolved experimentally, with the sole exception of SnF_4, for which $\Delta = 1.66$ mm/sec. The proposed structure of SnF_4, a layered inorganic polymer built of octahedra with D_{4h} symmetry, is shown in Fig. 2. The presence of a rather strong quadrupole splitting in this case—in contrast to all the others—can be explained by a particularly substantial difference in the degree of ionicity of the four sp^2d-hybridized Sn—F bonds to the F atoms lying in the principal plane of the polymer and forming bridging bonds between Sn atoms, and the two other $(p_z d_{z^2})$ SnF bonds, which are apparently ionic to a significant extent. In going from SnF_4 to K_2SnF_6 and Cs_2SnF_6, i.e., from an octahedron with D_{4h} symmetry to O_h with six equivalent (sp^3d^2) Sn—F bonds, the quadrupole splitting disappears. At the same time, the increase in the degree of symmetry of the molecule is accompanied by a strong decrease in the Debye-Waller factor—especially at room temperature—whereas the chemical shift remains unchanged.

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1. V. I. Goldanskii, *The Mössbauer Effect and Its Applications in Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1963.
2. V. I. Goldanskii, E. F. Makarov et al., DAN, **151**, 357 (1963).

3. V. I. Goldanskii, E. F. Makarov, V. V. Khrapov, Third Conference on the Mössbauer Effect, USA, Ithaca, September 1963.

4. F. L. Shapiro, UFN, **72**, 685 (1960).

5. Yu. M. Kagan, ZhETF, **41**, 659 (1961).

6. R. E. Watson, A. J. Freeman, Phys. Rev., **120**, 1125 (1960).

7. L. R. Walker, G. K. Wertheim, V. Jaccarino, Phys. Rev. Lett., **6**, 98 (1961).

8. T. N. Sumarokova, D. S. Sakenova, ZhOKh, **32**, 3 (1962).

9. B. F. Ormont, *Structures of Inorganic Substances*, Moscow-Leningrad, 1950, p. 520.

10. V. I. Goldanskii, T. M. Gorodinskii et al., DAN, **147**, 127 (1961).

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