

Vibrational and ^{119}Sn Mössbauer spectra of tin(IV) halide complexes with 1,3-dimethylurea and 1,3-dimethylthiourea

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Abstract

Tin(IV) halide complexes with 1,3-dimethylurea (dmu) and 1,3-dimethylthiourea (dmu) have been prepared and characterised by IR, Raman and ^{119}Sn Mössbauer spectroscopies. The previously reported isomer shift (IS) values of $\text{SnBr}_4(\text{dmu})_2$ and $\text{SnI}_4(\text{dmu})_2$ have been revised to 0.98 and 1.32 mm s^{-1} , respectively. The IS increases with decreasing electronegativity of the halogen atoms, and on going from dmu to dmtu complexes. The variation of the IS of SnX_4L_2 complexes with the electronegativity of the halogen X and the donor atom of the ligand L is studied. The IS can be used to get information about the atoms bonded to tin. The shifts of $\nu(\text{C}=\text{E})$ ($\text{E}=\text{O}, \text{S}$) and $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})$ with respect to the free ligands, in the IR spectra of the complexes, indicate that the dmu and dmtu ligands coordinate through the O and S atoms, respectively. The structure of the complexes is discussed in terms of the Mössbauer quadrupole splitting and the tin-halogen stretching vibrations in the IR and Raman spectra.

Introduction

The ^{119}Sn Mössbauer isomer shift (IS) reflects the s electron density at the tin nucleus, and is sensitive to the electronegativities of the atoms bonded to tin. In fact, it is well known that within a homologous series of tin(IV) compounds, the Mössbauer IS values are correlated to the partial atomic charges on tin (Q_{Sn}), with higher IS for small Q_{Sn} values [1–3]. In the case of octahedral tin(IV) halide complexes, SnX_4L_2 , the IS should be sensitive to the electronegativity of both X and L. Indeed, linear relationships between the IS and the electronegativity of X have been reported for tin(IV) complexes with 2,2'-bipyridine [4], *N,N*-dimethylformamide [5], dimethyl sulfoxide [5] and pyridine [6]. The nature of the donor atom in the ligand L should also affect the IS . In agreement with this idea, it was early noted that the IS varied with the donor atom in the general order $\text{O} < \text{N} < \text{S} < \text{P}$ [7], and a correlation table could be constructed [8]. In fact, the IS has been used to determine the donor atom in SnX_4 complexes with organic ligands [9–11].

The average IS for 28 octahedral SnCl_4 complexes with S-donor ligands is 0.66 mm s^{-1} (standard deviation 0.06 mm s^{-1}) [12]. Furthermore, the IS of SnBr_4 and SnI_4 complexes are *c.* 0.27 and 0.64 mm s^{-1} higher than for SnCl_4 complexes, respectively [13]. Therefore, we can expect IS values of about 0.93 and 1.30 mm s^{-1} , respectively, for octahedral SnBr_4 and SnI_4 complexes with S-donor ligands. On the other hand, the IS values reported for $\text{SnBr}_4(\text{dmu})_2$ and $\text{SnI}_4(\text{dmu})_2$ ($\text{dmu} = 1,3\text{-dimethylthiourea}$) are 0.40 and 0.41 mm s^{-1} , respectively [14]. These IS values are surprisingly close to each other and anomalously low, as the IR spectra indicate that the ligands are coordinated through the S atom [14]. Consequently, if Mössbauer spectroscopy can yield information about the atoms bonded to tin, the IS values reported for $\text{SnX}_4(\text{dmu})_2$ ($\text{X} = \text{Br}, \text{I}$) should be wrong. For this reason, we have repeated Mössbauer measurements on both compounds, as well as on the other compounds in the series $\text{SnX}_4(\text{dmu})_2$ and $\text{SnX}_4(\text{dmu})_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$; $\text{dmu} = 1,3\text{-dimethylurea}$). In this way, we can check the influence of both the halogen atom and the donor atom of the ligand, on the IS . The compounds are also characterised by means of the Mössbauer quadrupole splitting (QS) and the IR and Raman spectra.

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Experimental

Reactions were carried out at room temperature under N_2 , using dry solvents purified by standard methods. $SnF_4(MeCN)_2$ [13] and SnX_4 ($X=Cl, Br, I$) [15] were prepared as previously reported. $SnCl_4$ was distilled and SnX_4 ($X=Br, I$) were sublimed *in vacuo*, immediately before use. The ligands dmtu and dmu (Aldrich) were used as received.

SnF_4L_2 ($L=dmtu, dmu$) complexes were prepared by stirring a suspension of $SnF_4(MeCN)_2$ in MeCN with a solution of the ligand (7–10% excess) in the same solvent, for 24 h. The rest of the complexes were precipitated by adding dropwise, with stirring, $SnCl_4$ on a solution of the ligand in CH_2Cl_2 , or adding a solution of the ligand in CH_2Cl_2 on a solution of SnX_4 ($X=Br, I$) in the same solvent. All the complexes were filtered off, washed with solvent and vacuum dried. Melting points and analytical data are collected in Table 1. The complexes are white except for $SnBr_4(dmtu)_2$ (yellow) and both SnI_4 complexes (brown). $SnCl_4(dmtu)_2$ has been reported to be yellow [14], but we have obtained it as a white powder. Although most of the complexes are reasonably stable in air, $SnI_4(dmu)_2$ is air sensitive and thermally unstable.

C, H and N microanalyses were carried out with a Perkin-Elmer 2400 CHN elemental analyser. The IR spectra were recorded on a Nicolet 5DX FT-IR instrument in the range $4000\text{--}250\text{ cm}^{-1}$, using Nujol mulls between CsI windows. The IR spectra of $SnBr_4L_2$ ($L=dmtu, dmu$) were also recorded on a Nicolet 60SX FT-IR instrument in the range $500\text{--}100\text{ cm}^{-1}$, both as polyethylene pellets and Nujol mulls between polyethylene windows. Raman spectra were recorded on a Jarrell-Ash spectrophotometer, model 25-300, using a Kr^+ laser (5309 and 6471 \AA) with the powdered samples sealed in capillary tubes. Iodine containing compounds decomposed in the laser beam. The laser plasma lines were used for frequency calibration [16]. Mössbauer spectra at liquid N_2 temperature were obtained using the system and conditions described previously [17].

The isomer shifts are referred to $BaSnO_3$ at room temperature, and the reproducibility of the Mössbauer parameters was $\pm 0.02\text{ mm s}^{-1}$.

Results and discussion

Mössbauer isomer shifts

The Mössbauer spectra of $SnBr_4(dmu)_2$ and $SnX_4(dmtu)_2$ ($X=Br, I$) are shown in Fig. 1, and the Mössbauer parameters of all the complexes studied are collected in Table 1. The IS values for $SnBr_4(dmtu)_2$ and $SnI_4(dmtu)_2$ are very close to our expected values for complexes with S-donor ligands, and much higher than those previously reported [14]. Consequently, dmtu coordinates through the S atom, in agreement with the conclusions from IR spectroscopy (see below and ref. 14). The important point, however, is the confirmation that the IS can be used to get information about the atoms bonded to tin. Indeed, Fig. 1 and Table 1 show that the IS increases with decreasing electronegativity of the halogen atoms, and on going from dmu to dmtu complexes. This is clearly shown in Fig. 2, where the IS values have been plotted against the Mulliken electronegativity of the halogen atoms (F, 4.438; Cl, 3.535; Br, 3.236; I, 2.880) [18]. Both linear plots show a similar slope. For that reason, we have studied the correlation of IS with the average Mulliken electronegativity of the halogen atoms for tin(IV) halide and mixed halide complexes. In order to get a broad range of electronegativity, we have considered only series where the IS of SnF_4L_2 was available, and the results are collected in Table 2. All the correlations are reasonably linear (as judged by the correlation coefficients) and the slopes are in a narrow range, thus suggesting a similar behaviour for all the series of complexes. Nevertheless, when organotin compounds are considered, the IS is much less sensitive to the electronegativity of the halogen atoms. Indeed, the IS values of $K_2[SnMe_2F_4]$, $Cs_2[SnMe_2Cl_4]$ and $Cs_2[SnMe_2Br_4]$ are 1.38, 1.63 and

TABLE 1. Analytical^a and Mössbauer data

| Compound | m.p. (°C) | C (%) | H (%) | N (%) | IS (mm s ⁻¹) | QS (mm s ⁻¹) | Γ (mm s ⁻¹) |
|------------------|-------------------------|------------|----------|------------|----------------------------|----------------------------|--------------------------------|
| $SnF_4(dmtu)_2$ | 186–187(d) | 17.6(17.9) | 3.8(4.0) | 13.3(13.9) | 0.09 | | 1.11 |
| $SnCl_4(dmtu)_2$ | 204–206(d) ^b | 15.5(15.4) | 3.5(3.4) | 11.9(11.9) | 0.73 | 0.34 | 0.92 |
| $SnBr_4(dmtu)_2$ | 192–193(d) ^c | 11.2(11.1) | 2.5(2.5) | 8.7(8.7) | 0.98 | 0.30 | 0.96 |
| $SnI_4(dmtu)_2$ | 132–133(d) ^d | 8.7(8.6) | 1.5(1.9) | 6.4(6.7) | 1.32 | 0.37 | 0.81 |
| $SnF_4(dmu)_2$ | 236–237 | 18.9(19.4) | 3.9(4.3) | 14.5(15.1) | –0.29 | 0.66 | 0.99 |
| $SnCl_4(dmu)_2$ | 213–215 ^e | 16.7(16.5) | 3.6(3.7) | 13.0(12.8) | 0.34 | 0.77 | 0.97 |
| $SnBr_4(dmu)_2$ | 189–191(d) | 11.8(11.7) | 2.6(2.6) | 9.1(9.1) | 0.59 | 0.44 | 0.91 |
| $SnI_4(dmu)_2$ | 37–39(d) | 9.0(9.0) | 2.0(2.0) | 6.7(7.0) | ^f | ^f | ^f |

^aCalculated values in parentheses. ^bReported as 202 °C [14]. ^cReported as 192 °C [14]. ^dReported as 109 °C [14]. ^eReported as 208 °C [14]. ^fThe sample decomposed before the Mössbauer spectrum could be recorded.

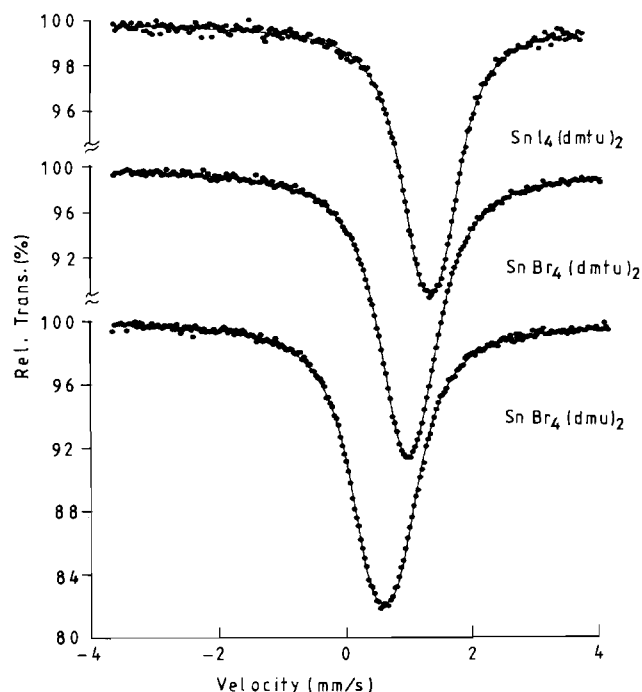


Fig. 1. Mössbauer spectra of $\text{SnBr}_4(\text{dmu})_2$ and $\text{SnX}_4(\text{dmtu})_2$ ($\text{X} = \text{Br}, \text{I}$).

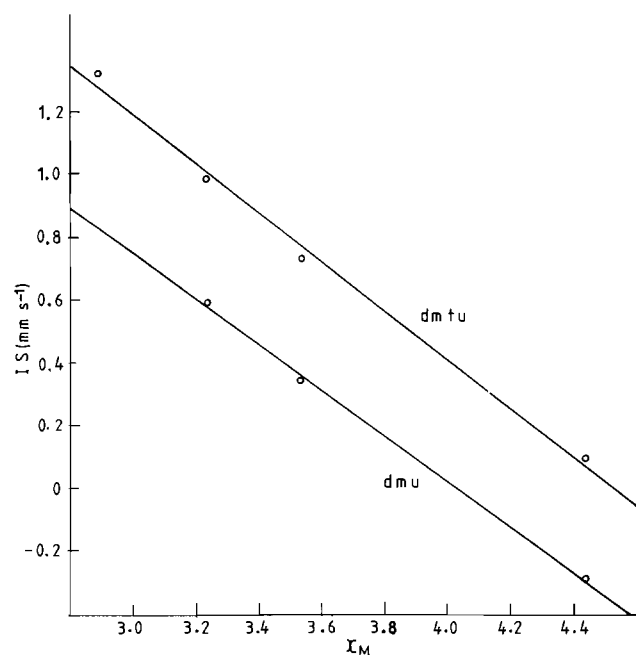


Fig. 2. Plot of IS vs. the average Mulliken electronegativity of the halides for tin(IV) halide complexes with dmtu and dmu .

1.76 mm s^{-1} , respectively [22], which lead to a slope of -0.31 ± 0.03 ($r = 0.995$).

As shown in Fig. 2, on going from dmu to dmtu complexes, the IS values increase by $c. 0.39 \text{ mm s}^{-1}$. More generally, while the average IS of SnCl_4 complexes with S-donor ligands is 0.66 mm s^{-1} (standard deviation

TABLE 2. Correlations of IS vs. average Mulliken electronegativity of the halogen atoms for octahedral tin(IV) halide and mixed halide complexes

| Ligand | No. points | r | slope ^a | IS refs. |
|---------------|------------|-------|--------------------|---------------|
| dmtu | 4 | 0.997 | $-0.78(5)$ | this work |
| dmu | 3 | 0.999 | $-0.72(2)$ | this work |
| detu | 4 | 0.997 | $-0.81(5)$ | 12 |
| Py | 10 | 0.995 | $-0.76(4)$ | 6 |
| DMF | 4 | 0.999 | $-0.77(2)$ | 5, 13, 19 |
| DMSO | 6 | 0.998 | $-0.76(3)$ | 5, 13, 19, 20 |
| MeCN | 4 | 0.990 | $-0.80(6)$ | 13, 17a, 21 |
| THF | 4 | 0.996 | $-0.83(5)$ | 13, 17a |

^aStandard deviations in parentheses.

0.06 mm s^{-1}) [12], a review of the reference bank of the Mössbauer Effect Data Centre (University of North Carolina, USA) reveals that the average IS of SnCl_4 complexes with O-donor ligands is 0.37 mm s^{-1} (standard deviation 0.08 mm s^{-1}). When other donor atoms are considered, we find, in agreement with previous reports [7], that the IS of SnCl_4 complexes varies with the donor atom in the general order $\text{O} < \text{N} < \text{S} < \text{P} < \text{As}$, with average values (standard deviations in parentheses) of $0.37(0.08)$, $0.42(0.08)$, $0.66(0.06)$, $0.75(0.10)$ and $0.78(0.10) \text{ mm s}^{-1}$, respectively. Obviously, these ranges are strongly overlapped and some SnCl_4 complexes with O-donor ligands have IS values as high as 0.58 mm s^{-1} [23]. Nevertheless, in some cases, a correct understanding of the factors affecting the IS can yield information about the atoms bonded to tin. For example, taking into account the average IS values for SnCl_4 complexes with N-, P-, As-, O- and S-donor ligands, we can expect average IS values between 0.66 and 0.78 mm s^{-1} for SnCl_4 complexes with Se-donor ligands. In fact, IS values of $c. 0.74 \text{ mm s}^{-1}$ have been reported for a few complexes of this type [10]. Therefore, the IS of $\text{SnCl}_4(\text{Se}_4\text{N}_2)_2$ (0.43 mm s^{-1}) [24] strongly indicates that the Se_4N_2 ligand coordinates through a nitrogen atom.

Mössbauer quadrupole splittings

Although the point charge model predicts that the quadrupole splitting (QS) of $\text{trans-SnX}_4\text{L}_2$ complexes should be twice the QS of their cis isomers, the ratio of the QS values of several pairs of isomers is in the range 1.4 – 1.9 [19]. The QS values of the complexes studied are collected in Table 1. The QS values of the dmtu complexes are very small, and we were unable to compute the spectrum of $\text{SnF}_4(\text{dmtu})_2$ as an unresolved quadrupole doublet. The errors associated with the QS of $\text{SnX}_4(\text{dmtu})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are probably larger than those corresponding to the dmu complexes ($c. \pm 0.02 \text{ mm s}^{-1}$). The small partial quadrupole splitting (pqs) of dmtu means that the QS cannot be used to get information about the geometry of $\text{SnX}_4(\text{dmtu})_2$

complexes. The same situation was found for $\text{SnX}_4(\text{detu})_2$ complexes ($\text{detu} = 1,3\text{-diethylthiourea}$) [12]. In the case of dmu complexes, on the other hand, the QS values of $\text{SnCl}_4(\text{dmu})_2$ (0.77 mm s^{-1}) and $\text{SnBr}_4(\text{dmu})_2$ (0.44 mm s^{-1}) strongly suggest that the SnCl_4 complex has a *trans* geometry, while $\text{SnBr}_4(\text{dmu})_2$ has a *cis* structure. Interestingly, a QS of 0.83 mm s^{-1} had been previously reported for $\text{SnBr}_4(\text{dmu})_2$ [25]. This indicates that Calógero *et al.* had obtained the *trans* isomer [25], in agreement with the idea that some factors, as yet not fully understood, govern the formation of either isomer and the transformation from one into the other [19]. According to the correlations between the tin–halogen distance and QS data for SnCl_4L_2 [26, 27] and SnBr_4L_2 complexes [28], we can expect the average bond distances of *c.* 2.39 and 2.55 Å for *trans*- $\text{SnCl}_4(\text{dmu})_2$ and $\text{SnBr}_4(\text{dmu})_2$ (both *cis* and *trans*), respectively. The QS of $\text{SnF}_4(\text{dmu})_2$ is intermediate between those of *trans*- $\text{SnCl}_4(\text{dmu})_2$ and *cis*- $\text{SnBr}_4(\text{dmu})_2$, and it is difficult to assign a structure on the basis of the QS alone.

Infrared and Raman spectra

Coordination through the S or O atoms in thiourea or urea type ligands should be reflected in an increase in $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})$ and decrease in $\nu(\text{C}=\text{E})$ ($\text{E} = \text{S}, \text{O}$) with respect to the free ligands [14, 29]. In free dmu $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})$ appears at 1566 cm^{-1} and $\nu(\text{C}=\text{S})$ at 722 cm^{-1} [14]. For dmu , on the other hand, $\nu(\text{C}=\text{O})$ and $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})$ are severely mixed with other modes giving rise to the so called amide I and amide II bands [30], and their positions are dependent on the state of the sample [31]. Bearing in mind the existence of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, the spectra of dilute CHCl_3 solutions ($\nu(\text{C}=\text{O}) = 1673 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{N}-\text{C}-\text{N}) = 1533 \text{ cm}^{-1}$) are a good approximation to the spectrum of the free ligand [31]. The relevant vibrations of the complexes studied are collected in Table 3 and show that the ligands coordinate through the S or O atoms. As found previously for other thioureas [29], the shifts in $\nu(\text{C}=\text{S})$ are very modest because of coupling with other vibrations. Although the tin–ligand bond strength in SnX_4L_2 is expected to increase from $\text{X} = \text{I}$ to $\text{X} = \text{F}$, only $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})$ in the dmu complexes follows the expected trend. The reasonably good behaviour of $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})$ in thiourea complexes has already been noted [29].

We can get information about the geometry around the tin atom by means of the tin–halogen stretching vibrations. According to group theory, four $\nu(\text{Sn}-\text{X})$ are both IR and Raman active for *cis*- SnX_4L_2 (C_{2v} symmetry) complexes, while only one IR (E_u) and two Raman (A_{1g} and B_{1g}) $\nu(\text{Sn}-\text{X})$ are expected for the *trans* isomer (D_{4h} symmetry) [32]. The data in Table 3 show that while $\text{SnCl}_4(\text{dmu})_2$ has a *cis* structure,

TABLE 3. Relevant vibrational bands (cm^{-1})

| Compound | $\nu(\text{C}=\text{S})^a$ or $\nu(\text{C}=\text{O})$ | $\nu_{\text{as}}(\text{N}-\text{C}-\text{N})^a$ | $\nu(\text{Sn}-\text{X})$ | |
|-------------------------------|---|---|---|-----------------------|
| | | | IR | Raman |
| $\text{SnF}_4(\text{dmu})_2$ | 722m, s | 1609vs | b | b |
| $\text{SnCl}_4(\text{dmu})_2$ | 720m | 1601vs | 343m 317s 303sh 289sh 282vs | 336m 299s 286vs |
| $\text{SnBr}_4(\text{dmu})_2$ | 716m | 1598s | 207vs | 190vs 159s 148s |
| $\text{SnI}_4(\text{dmu})_2$ | 713s | 1597s | c | c |
| $\text{SnF}_4(\text{dmu})_2$ | 1629vs | d | 597m 552vs 532vs | 550m |
| $\text{SnCl}_4(\text{dmu})_2$ | 1607vs | d | 330vs | 319vs 249m |
| $\text{SnBr}_4(\text{dmu})_2$ | 1604vs | 1572vs | 234vs 215vs | 201vs 180m |
| $\text{SnI}_4(\text{dmu})_2$ | 1616vs | 1578vs | c | c |

^aIR spectrum. ^bBands at 544, 517 and 501 cm^{-1} in the IR spectrum ($544, 512$ and 499 cm^{-1} in the Raman spectrum) cannot be assigned unambiguously as $\nu(\text{Sn}-\text{F})$ because of the presence of ligand absorptions in the same region. ^cNot recorded.

^dObscured by $\nu(\text{C}=\text{O})$.

$\text{SnCl}_4(\text{dmu})_2$ has the *trans* geometry proposed on the basis of the Mössbauer QS . For both compounds, the bands appear in the regions expected from the correlations between QS and $\nu(\text{Sn}-\text{Cl})$ for *cis* [33] and *trans* [19] SnCl_4L_2 complexes. The QS in *cis*- $\text{SnCl}_4(\text{dmu})_2$ is positive because the average $\nu(\text{Sn}-\text{Cl})$ calculated from $QS = 0.34 \text{ mm s}^{-1}$ is 306 cm^{-1} [33] in good agreement with the experimental value (311 cm^{-1}), while $QS = -0.34 \text{ mm s}^{-1}$ would correspond to an average $\nu(\text{Sn}-\text{Cl})$ of *c.* 272 cm^{-1} [33]. In addition, the calculated A_1 mode (278 cm^{-1}) [33] is also in good agreement with the experimental value of *c.* 285 cm^{-1} . For *trans*- $\text{SnCl}_4(\text{dmu})_2$, on the other hand, QS is negative as $QS = -0.77 \text{ mm s}^{-1}$ leads to the calculated average $\nu(\text{Sn}-\text{Cl})$ and E_u frequencies of 307 and 333 cm^{-1} , respectively [19], in excellent agreement with the experimental values of 307 and 330 cm^{-1} . For $QS = 0.77 \text{ mm s}^{-1}$ the calculated average $\nu(\text{Sn}-\text{Cl})$ is 279 cm^{-1} [19]. *trans*- $\text{SnCl}_4(\text{dmf})_2$ ($\text{dmf} = N,N\text{-dimethylformamide}$) has very similar QS [19] and $\nu(\text{Sn}-\text{Cl})$ [34] values to those corresponding to *trans*- $\text{SnCl}_4(\text{dmu})_2$, which indicates that dmf and dmu have similar donor strength with respect to SnCl_4 . The IR and Raman spectra of

$\text{SnBr}_4(\text{dmu})_2$ are consistent with a *cis* structure, as proposed from the Mössbauer *QS*, and $\nu(\text{Sn}-\text{Br})$ are very similar to those reported for *cis*- $\text{SnBr}_4(\text{dmf})_2$ [34], in agreement with the identical *QS* of both compounds [19]. The spectra of $\text{SnF}_4(\text{dmu})_2$ seem to be consistent with a *cis* structure also. The spectra of $\text{SnBr}_4(\text{dmu})_2$, however, do not lead to an unambiguous structural assignment. While the Mössbauer *QS* is very similar to that corresponding to $\text{SnCl}_4(\text{dmu})_2$, thus pointing to a *cis* structure, the vibrational spectra are suggestive of a *trans* structure, with splitting of the B_{1g} mode due to solid state effects. Nevertheless, the positions of the E_u and A_{1g} modes are not consistent with the *QS* value according to the correlations for *trans*- SnBr_4L_2 complexes [28].

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