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Note

cis–trans Isomerism in tetrabromobis(1,3-dimethylurea)tin(IV)

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Abstract

trans-$SnBr_4(dmu)_2$ (dmu = 1,3-dimethylurea) has been prepared by heating the *cis* isomer, and both compounds have been characterized by IR, Raman and ^{119}Sn Mossbauer spectroscopies. The Mossbauer quadrupole splitting (*QS*) of the *trans* isomer is only 1.7 times the *QS* of the *cis* isomer and the average of the vibrational ν(Sn–Br) frequencies is higher for the *cis* isomer. These facts indicate that the tin–ligand bond is stronger for the *trans* isomer, and that the partial quadrupole splitting of the dmu ligand is more positive (weaker donor) when it coordinates in the *cis* positions. A similar situation is found for other pairs of *cis*- and *trans*-SnX_4L_2 isomers.

Introduction

We have reported recently a vibrational and ^{119}Sn Mössbauer study of tin(IV) halide complexes with 1,3-dimethylurea (dmu) and 1,3-dimethylthiourea (dmtu) [1]. The Mössbauer quadrupole splitting (*QS*) values of $SnCl_4(dmu)_2$ (0.77 mm s^{-1}) and $SnBr_4(dmu)_2$ (0.44 mm s^{-1}) strongly suggest that the $SnCl_4$ complex has a *trans* geometry, while $SnBr_4(dmu)_2$ has a *cis* structure. Indeed the IR and Raman spectra support these structure assignments [1]. Nevertheless, a *QS* of 0.83 mm s^{-1} had been previously reported for $SnBr_4(dmu)_2$ [2]. Bearing in mind that the point charge model predicts that the *QS* of octahedral *trans*-SnX_4L_2 should be twice the *QS* of the corresponding *cis* isomer [3], the *QS* data suggest that $SnBr_4(dmu)_2$ might present *cis–trans* isomerism. In fact, a few pairs of *cis–trans* isomers have been characterized by vibrational [4, 5] and Mössbauer [6, 7] spectroscopies, and the phenomenon has been confirmed crystallographically for $SnBr_4(OPPh_3)_2$ [7]. On the basis of vibrational and *QS* data, we have suggested that the Sn–L bond is stronger for *trans*-SnX_4L_2 compounds than for their *cis* isomers [6, 7]. In order to further check this suggestion and to understand the different *QS* values reported for $SnBr_4(dmu)_2$ [1, 2], we have prepared both *cis*- and *trans*-$SnBr_4(dmu)_2$ and characterized them by vibrational and ^{119}Sn Mössbauer spectroscopies.

Experimental

The synthesis of *cis*-$SnBr_4(dmu)_2$ has been described previously [1]. *trans*-$SnBr_4(dmu)_2$ was prepared by heating the *cis* isomer in a sealed tube for 19 h at 119 °C. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR instrument, using Nujol mulls between CsI windows. Raman spectra were recorded on a Jarrell-Ash spectrophotometer, model 25-300, using an Ar^+ (4880 Å) laser with the samples sealed in capillary tubes. Mössbauer spectra at liquid N_2 temperature were obtained using the system and conditions described previously [8]. The isomer shift (*IS*) values are referred to $BaSnO_3$ at room temperature, and the reproducibility of the Mossbauer parameters was ±0.02 mm s^{-1}.

Results and discussion

As reported for other tin(IV) halide complexes [5, 7], heating *cis*-$SnBr_4(dmu)_2$ transforms it into the *trans* isomer. Both isomers are readily distinguished by means of their Mössbauer spectra (Fig. 1) which show a resolved doublet for the *trans* isomer and a broad single line for the *cis* compound. Nevertheless, it must be stressed that, if only one isomer is available, the resolvable or unresolvable nature of the Mossbauer doublets cannot be used for structural assignments [9, 10]. The Mössbauer parameters of *cis*- and *trans*-$SnBr_4(dmu)_2$ are collected in Table 1 with some selected vibrational data. The Mössbauer parameters reported previously for $SnBr_4(dmu)_2$ ($IS = 0.69$, $QS = 0.83$ mm s^{-1}) [2] are close to those of the *trans* isomer, and the small differences are not unexpected for inter-laboratory comparisons. Table 1 shows that both *cis*- and *trans*-$SnBr_4(dmu)_2$ have the same *IS* values, as observed for other pairs of isomers [6]. Furthermore, the *IS* values

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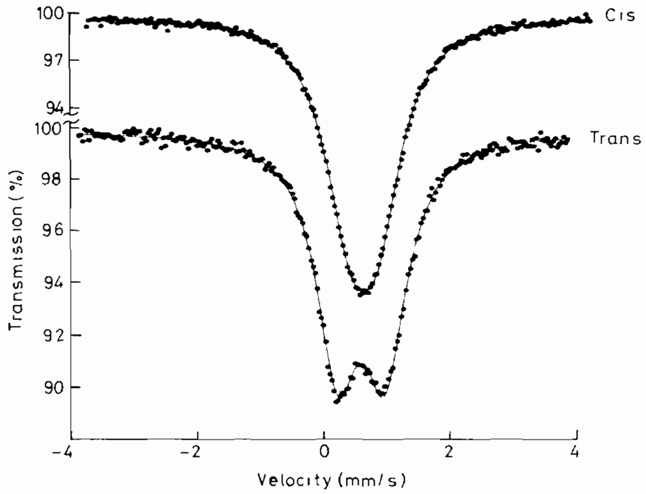

Fig. 1. Mossbauer spectra of *cis*- and *trans*-$SnBr_4(dmu)_2$

TABLE 1 Spectroscopic data for *cis*- and *trans*-$SnBr_4(dmu)_2$

Technique	*cis*	*trans*	Parameter or assignment
Mossbauer (mm s^{-1})	0.59	0.59	*IS*
	0.44	0.76	*QS*
	0.91	0.82	Γ
IR (cm^{-1})	3404m	3405m	ν(N–H)
	3365m	3377m	ν(N–H)
	1604vs	1614vs	ν(C=O)
	1573vs	1584vs	ν_{as}(N–C–N)
	405m		ν(Sn–O)
		402s	ν(Sn–O) (A_{2u})
		237vs	ν(Sn–Br) (E_u)
	232vs		ν(Sn–Br) (B_1)
	214vs		ν(Sn–Br) (B_2)
Raman (cm^{-1})	405vw		ν(Sn–O)
	399vw		ν(Sn–O)
		397vw	ν(Sn–O) (A_{1g})
	202vvs		ν(Sn–Br) (A_1)
	181s		ν(Sn–Br) (A_1)
		194vvs	ν(Sn–Br) (A_{1g})
		149m	ν(Sn–Br) (B_{1g})

are in the range expected for an octahedral $SnBr_4$ complex with two O-donor ligands, bearing in mind that the average *IS* for $SnCl_4$ complexes with O-donor ligands is 0.37 mm s^{-1} (standard deviation 0.08 mm s^{-1}) [1], and that the average difference between the *IS* of $SnBr_4L_2$ and $SnCl_4L_2$ is 0.27 mm s^{-1} (standard deviation 0.07 mm s^{-1}) [11]. Indeed, the *IS* is 0.25 mm s^{-1} higher than for *trans*-$SnCl_4(dmu)_2$ [1], and both *trans*-$SnX_4(dmu)_2$ (X = Cl, Br) have essentially the same *QS* in agreement with the identical partial quadrupole splitting (*pqs*) of Cl and Br [3].

According to the point charge model, the Mossbauer *QS* of *trans*-SnX_4L_2 compounds should be twice the *QS* of the corresponding *cis* isomers [3]. Instead, the ratio *QS*(*trans*)/*QS*(*cis*) has been found in the range 1.4–1.9 for the pairs of isomers which have been studied by Mossbauer spectroscopy [6, 7]. Likewise, the ratio *QS*(*trans*)/*QS*(*cis*) for $SnBr_4(dmu)_2$ is 1.7 (see Table 1). Bearing in mind that dmu [1], as well as the other ligands involved [6, 7], has a positive *pqs*, the ratios *QS*(*trans*)/*QS*(*cis*) < 2 indicate that the *pqs* of the ligands is not constant, but it is more positive (weaker donors) when the ligands coordinate in the *cis* positions [6]. There is some evidence that also ligands with negative *pqs* values (strong donors) coordinate more strongly in *trans* positions. For example, the $^1J(^{119}Sn–^{31}P)$ NMR coupling constant of *trans*-$SnBr_4(PMePh_2)_2$ is 1730 Hz, while it is only 480 Hz for the chelate $SnBr_4$(dppe) (dppe = bis(diphenylphosphinoethane)), which points to a stronger Sn–P bond for the former compound [12]. Therefore, we expect a ratio *QS*(*trans*)/*QS*(*cis*) > 2 for ligands, such as phosphines, with negative *pqs* values [10]. On the other hand, the stronger donor power of ligands in *trans* position should be accompanied by a lengthening of the Sn–Br bonds in *trans*-$SnBr_4L_2$ complexes. This expectation has been confirmed crystallographically for *cis*- and *trans*-$SnBr_4(OPPh_3)_2$ [7], but in the case of *cis*- and *trans*-$SnBr_4(dmu)_2$, the difference between the average Sn–Br distances should be very small. Indeed, we have reported a linear relationship between the average Sn–Br distance and the *pqs* of the ligands for $SnBr_4L_2$ complexes [13], and according to the best least-squares fit (eqn. (1)) [7], the calculated average distances are 2.553 and 2.558 Å for *cis*- and *trans*-$SnBr_4(dmu)_2$, respectively.

$$d(\text{Sn–Br}) = (-0.047 \pm 0.002)\ (4\ pqs) + (2.594 \pm 0.004)\ (\text{Å}) \qquad (1)$$

The IR spectra of *cis*- and *trans*-$SnBr_4(dmu)_2$ (Table 1) show that the ligands coordinate in a similar way in both compounds, and the increase in ν_{as}(N–C–N) and decrease in ν(C=O) with respect to the free ligand (1533 and 1671 cm^{-1}, respectively) [14], confirm coordination through the O atom. According to group theory, two ν(Sn–O) ($A_1 + B_1$) and four ν(Sn–Br) (2 $A_1 + B_1 + B_2$) are both IR and Raman active for *cis*-$SnBr_4(dmu)_2$ (idealized C_{2v} symmetry), while one ν(Sn–O) (A_{2u}) and one ν(Sn–Br) (E_u) are IR active and one ν(Sn–O) (A_{1g}) and two ν(Sn–Br) ($A_{1g} + B_{1g}$) modes are Raman active for *trans*-$SnBr_4(dmu)_2$ (idealized D_{4h} symmetry) [15]. Although we cannot distinguish unambiguously between the two ν(Sn–O) modes of *cis*-$SnBr_4(dmu)_2$, all the skeletal stretching vibrations are assigned in Table 1. For *trans*-$SnBr_4L_2$ complexes, the ν(Sn–Br) frequencies can be calculated. Indeed, while the Raman active B_{1g} mode is not very sensitive to the ligand and appears around 150 cm^{-1}, the IR active E_u and the Raman active A_{1g} modes are linearly related to the Mossbauer *QS* [13]. According to these corre-

TABLE 2. ν(Sn–X) and *QS* data for *cis*- and *trans*-SnX_4L_2

L	X	ν(*cis*)[a]	ν(*trans*)[b]	Δν[c]	Ref.	*QS*(*trans*)/*QS*(*cis*)	Ref.
$HCONMe_2$	Cl	316	308	8	16	1.4	6
Ph_3PO	Br	210	203	7	7	1.4	7
Me_2SO	Cl	308	302	6	16	1.4	6
dmu	Br	207	204	3	this work	1.7	this work
$MeCONMe_2$	Cl	312	310	2	16	1.7	6
$HCONMe_2$	Br	210	209	1	5	1.9	6

[a] Average ν(Sn–Br) in cm^{-1}: $1/4(A_1+A_1+B_1+B_2)$. [b] Average ν(Sn–Br) in cm^{-1}: $1/4(2\,E_u+A_{1g}+B_{1g})$. [c] ν(*cis*) − ν(*trans*)

lations, *QS* is negative for *trans*-$SnBr_4(dmu)_2$, and the E_u and A_{1g} frequencies calculated from $QS = -0.76$ mm s^{-1} are 238 and 191 cm^{-1}, respectively, in excellent agreement with the experimental frequencies shown in Table 1. Interestingly, the average ν(Sn–Br) for *cis*-$SnBr_4(dmu)_2$ (207 cm^{-1}) is higher than for the *trans* isomer (204 cm^{-1}), in agreement with the higher donor power of the ligand in *trans* position suggested by the *QS* data. A similar behaviour has been observed for all the other *cis–trans* pairs for which data are available (Table 2). Although no meaningful correlation can be obtained from the data, Table 2 seems to indicate a trend of smaller *QS* ratios the higher the difference between the average ν(Sn–X) of the *cis* and *trans* isomers. The trend suggests that when ν(Sn–X) is identical for both isomers (i.e. when the ligand has the same donor power and *pqs* in both isomers), the *QS* ratio should be close to the value of 2 predicted by the point charge model [3]. However, it should be remembered that any relationship involving ν(Sn–X) can fail for some compounds if those modes are strongly coupled to other vibrations. Similarly, ν(Sn–L) vibrations are normally highly coupled with other modes of the ligand and the skeleton SnX_4L_2 [16]. For that reason, the ν(Sn–O) frequencies are higher for *cis*- than for *trans*-$SnBr_4(dmu)_2$ (see Table 1), although the *QS* and ν(Sn–Br) data indicate that the Sn–O bond must be stronger for the *trans* isomer.

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