First Crystallographically Authenticated Example of Cis–Trans Isomerism in Octahedral Tin(IV) Halide Complexes

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Introduction

Octahedral tin(IV) halide complexes, SnX4L2, usually have either the cis or the trans structure. Still, for some compounds, both isomers have been detected in solution by vibrational1 and NMR spectroscopies2,3 and in the solid state by vibrational,2,3 NQR,4 and Mössbauer5 spectroscopies. Nevertheless, cis–trans isomerism in octahedral tin(IV) halide complexes had not so far been confirmed crystallographically by solving the X-ray crystal structure of both isomers. Indeed, it would be very interesting to compare the structures of the cis and trans isomers. While, on the basis of nonbonded intramolecular van der Waals interactions, we expect bond angles closer to the regular octahedral ones for the trans isomers,6 we may wonder if the Sn–X and Sn–L bond distances should be identical for both isomers. In fact, Mössbauer spectroscopic evidence suggests that, at least for some compounds, they should be different. According to the point charge model, the Mössbauer quadrupole splitting (QS) of the trans isomer should be twice the QS of the corresponding cis isomer.9 Instead, the ratio QStrans/QScis has been found in the range 1.4–1.9 for the pairs of isomers which have been studied by Mössbauer spectroscopy.7 Bearing in mind that the ligands involved had a positive partial quadrupole splitting (pqs), the ratios QStrans/QScis < 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.7 We have recently reported linear relationships between the average Sn–X distance and the pqs of the ligands for octahedral tin(IV) chloride10 and bromide11 complexes. According to these correlations, the Sn–X distance should increase when the pqs of the ligands becomes more negative (stronger donors). Therefore, the Sn–X distance in SnX4L2 complexes should be longer when the ligands L coordinate in trans position. Consequently, a comparison of the crystal structures of both cis and trans isomers would allow us to check the reliability of quantitative structural information obtained from Mössbauer spectroscopy.

Aslanov and co-workers have reported the crystal structures of SnX4(OPPh3)2 (X = Cl, Br, I),12,13 While SnX4(OPPh3)2 (X = Cl, I) have a cis geometry,13 SnBr4(OPPh3)2 is trans.13 On the other hand, SnBr4(OPPh3)2 has a large dipole moment in dioxane solution,14 and three Sn–Br stretching frequencies have been assigned in its solid-state IR spectrum.15 Furthermore, SnCl4(OPPh3)2 and SnBr4(OPPh3)2 have been reported to be isomorphous.14 Therefore cis-SnBr4(OPPh3)2 might also exist. For that reason, we have tried to characterize both isomers and solve the X-ray structure of the cis complex.

Experimental Section

Infrared spectra (4000–210 cm−1) were recorded on a Perkin Elmer 1600 FT-IR instrument, using Nujol mulls between CaF2 windows. Raman spectra were recorded on a Jarrell Ash spectrophotometer, Model 25–300, using Ar+(5145 and 4880 Å) and Kr+(6471 and 5309 Å) lasers with the samples sealed in capillary tubes. Throughout the work, Raman spectroscopy was used to check whether any of the isomers or a mixture coordinate in the cis positions.
of them was formed. Mössbauer spectra at liquid N\textsubscript{2} temperature were obtained with use of the system and conditions described previously.

The isomer shifts are referred to BaSnO\textsubscript{3} at room temperature, and the reproducibility of the Mössbauer parameters was ±0.02 mm s\textsuperscript{-1}. Sample thickness in every case was 10 mg of natural tin cm\textsuperscript{-2}.

The synthesis of SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2} was performed under an atmosphere of dry nitrogen by mixing CHCl\textsubscript{3} solutions of SnBr\textsubscript{4} and Ph\textsubscript{3}PO in a 1:2 molar ratio at room temperature. The white solid was precipitated by addition of a very small amount of the cis compound, while vapor diffusion of diethyl ether on a mixture of SnBr\textsubscript{4} and Ph\textsubscript{3}PO yields essentially crystalline materials.

Mössbauer spectra at liquid N\textsubscript{2} temperature were obtained with use of the system and conditions described previously.

Preparation of cis-SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2}. Vacuum sublimation to a cold finger cooled with liquid N\textsubscript{2} afforded cis-SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2} IR (cm\textsuperscript{-1}): ν(SnBr) = 238 vs (B1), 220 vs (B1). Raman (cm\textsuperscript{-1}): ν(SnBr) = 221 m (B1), 204 vs (A\textsubscript{3}), 178 vs (A\textsubscript{1}). Mössbauer: IS = 0.62 mm s\textsuperscript{-1}, QS = 0.64, mm\textsuperscript{s}, Γ = 0.93 mm s\textsuperscript{-1}.

Preparation of trans-SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2}. A sublimed sample was heated in a sealed tube for 16 h at 126 °C, yielding trans-SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2}. IR (cm\textsuperscript{-1}): ν(SnBr) = 243 vs, 229 vs. Raman (cm\textsuperscript{-1}): ν(SnBr) = 189 vs (A\textsubscript{3}), 150 m (B\textsubscript{1}). Mössbauer: IS = 0.58 mm s\textsuperscript{-1}, QS = 0.89 mm s\textsuperscript{-1}, Γ = 0.86 mm s\textsuperscript{-1}.

X-ray structure determination. A summary of the fundamental data is given in Table I. A colorless prismatic crystal was mounted in an Enraf-Nonius CAD4 diffractometer. The cell dimensions were obtained by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for the non-hydrogen atoms and fixed isotropic temperature factors and positions for the H atoms, which were geometrically placed. In order to prevent bias (F) vs (F\textsubscript{o}) or (sin θ)/λ, the last steps of the refinement were carried out with weights calculated by means of PESOS. Most of the calculations were carried out with XRABO. The final atomic coordinates are given in Table II.

Syntheses and Spectra. As reported previously for other tin(IV) halide complexes which undergo cis-trans isomerization in the solid state, vacuum sublimation of SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2} yields the cis isomer, which transforms into the trans isomer on heating. Consequently, a mixture of isomers was obtained when the sublimate condensed on the walls just above the heating bath, but cis-SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2} was isolated when the sublimate was condensed at liquid nitrogen temperature. The solvent used also plays a major role in determining the isomer formed. So, while crystallization from a mixture of tetrahydrofuran and diethyl ether led to a mixture of the cis and trans isomers, crystallization from a mixture of chloroform and n-hexane yielded essentially the trans isomer.

According to group theory, four v(SnBr) bands are both IR and Raman active for cis-SnBr\textsubscript{4}L\textsubscript{2} (idealized C\textsubscript{2p} symmetry), while only one IR (B\textsubscript{1}) and two Raman (A\textsubscript{1} and B\textsubscript{2}) ν(SnBr) bands are expected for the trans isomer (idealized D\textsubscript{2h} symmetry). Although the IR active E\textsubscript{g} mode of trans-SnBr\textsubscript{4}(OPPh\textsubscript{3})\textsubscript{2} is split by solid-state effects, unambiguous structural assignments can be made from the IR and Raman spectra (see Experimental Section). Both isomers are also readily distinguished by means of their Mössbauer spectra (Figure 1) which show that the cis isomer in a mixture of tin(IV) halide complexes is generally less cis-sensitive than the trans isomer.

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and cis-SnBr₄(OPPh₃)₂ are isomorphous. In agreement with our expectations, the weighted average Sn-Br distance for SnBr₄(OPPh₃)₂ is shorter than for the trans isomer. Therefore, we expect that the OPPh₃ ligand has a more positive ratio d(Sn-Br) and indicates a shorter lengthening of the Sn-O bond and a shortening of the P-O bond going from the trans to the cis isomer. Unfortunately, no significant differences are observed in the P-O (1.516(8) Å for the cis and 1.516(9) Å for the trans isomer) and Sn-O distances (2.080(8) Å for the cis and 2.101(9) Å for the trans isomer).

The present results provide the first crystallographic authenticated example of cis–trans isomerism in octahedral tin(IV) halide complexes and support the usefulness of Mössbauer spectroscopy to gain insight into the nature of the tin–ligand bond. When the correlation between the Sn–Br distance and the pqs of the ligands for SnBr₄L₂ complexes was being studied, literature data were used for the Sn–Br distance and the Mössbauer QS of SnBr₄(OPPh₃)₂. While the crystal structure corresponded to the cis isomer, the QS (0.61 mm s⁻¹) is shown by the present results to correspond to the cis isomer. Therefore, it is clear that cis–trans isomerism in the solid state is more widely extended than usually assumed, and subtle changes can lead to the formation of either isomer or a mixture of them. Consequently, care should be taken to confirm that any property corresponds to a particular isomer. With the Sn–Br distances and pqs data included in ref 11, the correct QS of trans-SnBr₄(OPPh₃)₂ (0.89 mm s⁻¹), and the data for cis-SnBr₄(OPPh₃)₂, the relationship between the average Sn–Br distance (in Å) and the pqs of the ligands (in mm s⁻¹) for SnBr₄L₂ complexes is given by eq 1 (six points, r = 0.996).

\[ d(\text{Sn–Br}) = (-0.047 \pm 0.002)(4\text{pqs}) + (2.594 \pm 0.004) \]  

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**Supplementary Material Available:** Tables of hydrogen atom parameters, anisotropic thermal parameters, bond distances, and bond angles (Tables S1–S4) (5 pages). Ordering information is given on any current masthead page.

(28) Although the Sn–O distances do not seem to follow the expected trend, the difference is not statistically significant in terms of the standard deviations.