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

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cis- and *trans*-$SnBr_4(OPPh_3)_2$ have been prepared and characterized by IR, Raman, and ^{119}Sn Mössbauer spectroscopies. The Mössbauer quadrupole splitting (QS) of the trans isomer is only 1.4 times the QS of the cis isomer, thus suggesting that the partial quadrupole splitting of the Ph_3PO ligand is more positive (weaker donor) when it coordinates in the cis positions. The structure of *cis*-tetrabromobis(triphenylphosphine oxide)tin(IV) was determined by X-ray crystallography. The compound crystallizes in the monoclinic $C2/c$ space group with a = 14.152(5) Å, b = 13.213(2) Å, c = 19.859(6) Å, β = 95.20(2)°, and Z = 4. Refinement of 204 parameters with 1777 reflections gave $R = 0.050$ and $R_w = 0.047$. The present results, with the crystal structure of the trans isomer described in the literature, provide the first authenticated example of cis–trans isomerism in octahedral tin(IV) halide complexes. In agreement with the predictions from Mössbauer spectroscopy, the weighted average Sn–Br distance for *cis*-$SnBr_4(OPPh_3)_2$ (2.544(2) Å) is significantly shorter than that for its trans isomer (2.557(2) Å).

Introduction

Octahedral tin(IV) halide complexes, SnX_4L_2, usually have either the cis or the trans structure. Still, for some compounds, both isomers have been detected in solution by vibrational[2] and NMR spectroscopies[3,4] and in the solid state by vibrational,[2,5] NQR,[6] and Mössbauer[7] 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,[8] 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 isomers should be twice the QS of the corresponding cis isomers.[9] 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 Mössbauer spectroscopy.[7] Bearing in mind that the ligands involved had a positive partial quadrupole splitting (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.[7] We have recently reported linear relationships between the average Sn–X distance and the pqs of the ligands for octahedral tin(IV) chloride[10] and bromide[11] 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 SnX_4L_2 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 $SnX_4(OPPh_3)_2$ (X = Cl, Br, I).[12,13] While $SnX_4(OPPh_3)_2$ (X = Cl, I) have a cis geometry,[12] $SnBr_4(OPPh_3)_2$ is trans.[13] On the other hand, $SnBr_4(OPPh_3)_2$ 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, $SnCl_4(OPPh_3)_2$ and $SnBr_4(OPPh_3)_2$ have been reported to be isomorphous.[16] Therefore *cis*-$SnBr_4(OPPh_3)_2$ 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 CsI 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

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Table I. Crystallographic Data for *cis*-$SnBr_4(OPPh_3)_2$

formula	$C_{36}H_{30}Br_4O_2P_2Sn$
fw	994.9
space group	*C*2/*c* (No. 15)
a, Å	14.152(5)
b, Å	13.213(2)
c, Å	19.859(6)
β, deg	95.20(2)
V, Å^3	3698(2)
Z	4
d_{calc}, g cm^{-3}	1.787
T, K	295
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)
μ(Mo Kα), cm^{-1}	50.90
scan technique	ω/2θ
θ range, deg	1–25
data collcd	(–16,0,0) to (16,15,23)
no. of reflcns collcd	3601
no. of unique data	3256
no. of unique data, (I) > 2σ(I)	1777
R(int)	0.041
abs factors, max–min	1.234–0.787
variables	204
$R(F_o)$	0.050
$R_w(F_o)$	0.047
max shift/error	0.022

of them was formed. Mössbauer spectra at liquid N_2 temperature were obtained with use of 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 ±0.02 mm s^{-1}. Sample thickness in every case was 10 mg of natural tin/cm^2. The synthesis of $SnBr_4(OPPh_3)_2$ was performed under an atmosphere of dry nitrogen by mixing CH_2Cl_2 solutions of $SnBr_4$ and Ph_3PO in a 1:2 molar ratio at room temperature. The white solid was precipitated by addition of *n*-hexane and purified by vacuum sublimation in a glass column, yielding a mixture of the cis and trans isomers. Anal. Calcd for $SnBr_4(OPPh_3)_2$: C, 43.46; H, 3.04. Found: C, 43.57; H, 2.82. Vapor diffusion of *n*-hexane on a $CHCl_3$ solution yielded essentially crystals of the trans isomer with a very small amount of the cis compound, while vapor diffusion of diethyl ether on a tetrahydrofuran solution yielded a mixture of crystals of the cis and trans isomers. A crystal of the cis isomer from this mixture was selected for the crystal structure determination.

Preparation of *cis*-$SnBr_4(OPPh_3)_2$. Vacuum sublimation to a cold finger cooled with liquid N_2 afforded *cis*-$SnBr_4(OPPh_3)_2$. IR (cm^{-1}): ν(SnBr) = 238 vs (B_2), 220 vs (B_1). Raman (cm^{-1}): ν(SnBr) = 221 m (B_1), 204 vs(A_1), 178 vs (A_1). Mössbauer: IS = 0.62 mm s^{-1}, QS = 0.64, mm s^{-1}, Γ = 0.93 mm s^{-1}.

Preparation of *trans*-$SnBr_4(OPPh_3)_2$. A sublimed sample was heated in a sealed tube for 16 h at 126 °C, yielding *trans*-$SnBr_4(OPPh_3)_2$. IR (cm^{-1}): ν(SnBr(E_u)) = 243 vs, 229 vs. Raman (cm^{-1}): ν(SnBr) = 189 vs (A_{1g}), 150 m (B_{1g}). Mössbauer: IS = 0.58 mm s^{-1}, QS = 0.89 mm s^{-1}, Γ = 0.86 mm s^{-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 refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Sn, Br, and P were taken from ref 18.

The structure was solved by Patterson and Fourier methods. An empirical absorption correction[19] applied at the end of the isotropic refinement by using unit weights led to a conventional *R* value of 0.089. Final refinement was carried out with anisotropic temperature 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 on ⟨*F*⟩ vs ⟨F_o⟩ or ⟨(sin θ) /λ⟩, the last steps of the refinement were carried out with weights calculated by means of PESOS.[20] Most of the calculations were carried out with XRAY80.[21] The final atomic coordinates are given in Table II.

Table II. Atomic coordinates for *cis*-$SnBr_4(OPPh_3)_2$

atom	*x*	*y*	*z*
Sn	0.00000	0.14602(8)	0.25000
Br(1)	0.16775(8)	0.1612(1)	0.30608(6)
Br(2)	–0.0532(1)	0.0097(1)	0.32981(8)
O	0.0368(5)	0.2619(6)	0.1865(4)
P	0.0254(2)	0.3333(2)	0.1266(1)
C(11)	0.1418(8)	0.3606(9)	0.1010(5)
C(12)	0.155(1)	0.376(1)	0.0345(6)
C(13)	0.245(1)	0.402(1)	0.0179(9)
C(14)	0.317(1)	0.408(1)	0.066(1)
C(15)	0.304(1)	0.393(1)	0.1328(9)
C(16)	0.2133(1)	0.367(1)	0.1498(7)
C(21)	–0.0306(8)	0.4486(9)	0.1497(5)
C(22)	–0.1157(9)	0.443(1)	0.1744(7)
C(23)	–0.164(1)	0.527(1)	0.1903(9)
C(24)	–0.125(1)	0.621(1)	0.1794(9)
C(25)	–0.041(1)	0.628(1)	0.157(1)
C(26)	0.010(1)	0.541(1)	0.1404(8)
C(31)	–0.0460(8)	0.286(1)	0.0540(6)
C(32)	–0.1105(9)	0.344(1)	0.0155(6)
C(33)	–0.160(1)	0.309(1)	–0.0407(8)
C(34)	–0.145(1)	0.210(2)	–0.0621(7)
C(35)	–0.082(1)	0.150(1)	–0.0251(7)
C(36)	–0.030(1)	0.185(1)	0.0338(6)

Results and Discussion

Syntheses and Spectra. As reported previously for other tin(IV) halide complexes which undergo cis–trans isomerization in the solid state,[5] vacuum sublimation of $SnBr_4(OPPh_3)_2$ 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*-$SnBr_4(OPPh_3)_2$ 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 ν(SnBr) bands are both IR and Raman active for *cis*-$SnBr_4L_2$ (idealized C_{2v} symmetry) complexes, while only one IR (E_u) and two Raman (A_{1g} and B_{1g}) ν(SnBr) bands are expected for the trans isomer (idealized D_{4h} symmetry). Although the IR active E_u mode of *trans*-$SnBr_4(OPPh_3)_2$ 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 trans isomer has a higher QS. The isomer shift (IS) can be used to get information about the atoms bonded to tin,[22] and our values (0.62 and 0.58 mm s^{-1} for the cis and trans isomers, respectively)[23] are fully consistent with a $SnBr_4$ complex with two O-donor ligands. As observed for other cis–trans pairs,[7] the IS values of both isomers are not significantly different.

For octahedral SnX_4L_2 complexes, the vibrational Sn–X stretching frequencies are related to the Mössbauer QS.[7,11,24] According to the correlations for *trans*-$SnBr_4L_2$ complexes,[11] the QS = –0.89 mm s^{-1} for *trans*-$SnBr_4(OPPh_3)_2$[25] would correspond to ν(SnBr) values of 241 cm^{-1} for the E_u mode and 193 cm^{-1} for

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(25) Ph_3PO has a positive pqs,[10a,24] thus leading to a positive QS for *cis*-$SnBr_4(OPPh_3)_2$, and a negative value for the trans isomer.

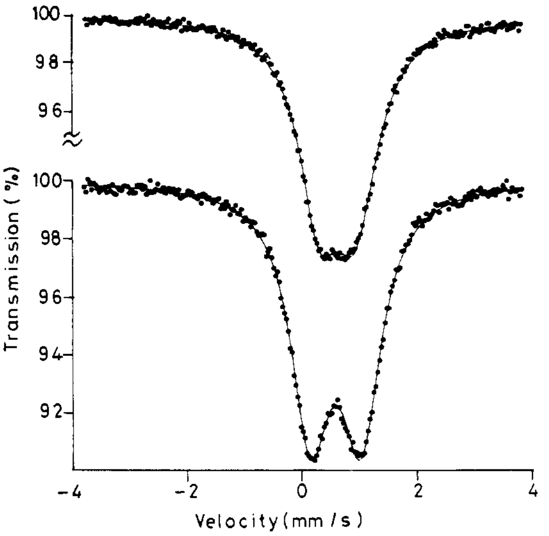

Figure 1. Mössbauer spectra of *cis*- (upper) and *trans*-$SnBr_4(OPPh_3)_2$ (lower).

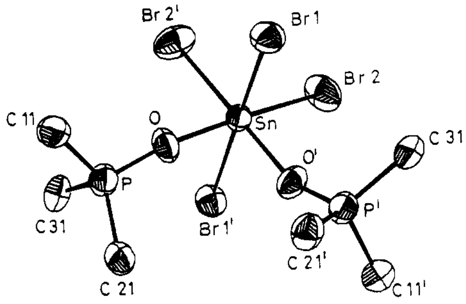

Figure 2. ORTEP drawing of *cis*-$SnBr_4(OPPh_3)_2$. The phenyl rings have been omitted for clarity.

A_{1g}, in good agreement with the experimental frequencies of 236 (average value) and 189 cm^{-1}, respectively. Interestingly, the average ν(SnBr) value is lower for the trans complex (203 cm^{-1}) than for the cis isomer (210 cm^{-1}). This result is consistent with the ratio QS_{trans}/QS_{cis} (1.4) being lower than 2, and indicates that the $OPPh_3$ ligand has a more positive pqs (weaker donor) when it coordinates in cis positions. Therefore, we expect that the average Sn–Br distance should be shorter for *cis*-$SnBr_4(OPPh_3)_2$ than for its trans isomer.[11]

X-ray Crystal Structure of *cis*-$SnBr_4(OPPh_3)_2$. An ORTEP drawing of *cis*-$SnBr_4(OPPh_3)_2$ is shown in Figure 2, and selected bond distances and angles are collected in Table III. As reported previously from X-ray powder photographs,[16] *cis*-$SnCl_4(OPPh_3)_2$[12a] and *cis*-$SnBr_4(OPPh_3)_2$ are isomorphous. In agreement with our expectations, the weighted average Sn–Br distance for *cis*-$SnBr_4(OPPh_3)_2$ (2.544(2) Å) is shorter than for the trans isomer (2.557(2) Å).[13] Although the difference is small, it can be considered as statistically significant.[26] This result supports the idea that the $OPPh_3$ ligand is a stronger donor when it coordinates in the trans positions, and it should be accompanied by a lengthening of the Sn–O bond and a shortening of the P-O bond on going from the trans to the cis isomer.[27] Unfortunately, no significant differences are observed in the P–O (1.515(8) Å for the cis and 1.516(9) Å[13] for the trans isomer) and Sn–O distances (2.080(8) Å for the cis and 2.101(9) Å[13] for the trans isomer).[28]

Table III. Selected Bond Lengths (Å) and Angles (deg) for *cis*-$SnBr_4(OPPh_3)_2$[a]

Sn–Br(1)	2.537(1)	Sn–Br(2)	2.557(2)
Sn–O	2.080(8)	P–O	1.515(8)
Br(1)–Sn–Br(1)′	170.92(7)	Br(2)–Sn–Br(2)′	90.45(5)
Br(1)–Sn–Br(2)	95.73(5)	Br(1)–Sn–Br(2)′	90.67(6)
O–Sn–O′	85.2(3)	Br(1)–Sn–O	86.1(2)
Br(1)–Sn–O′	87.2(2)	Br(2)–Sn–O	176.7(2)
Br(2)–Sn–O′	92.2(2)	Sn–O–P	156.9(5)

[a] Symmetry code (′): $\bar{x}, y, {}^1/_2 - z$.

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 $SnBr_4L_2$ complexes was being studied,[11] literature data were used for the Sn–Br distance and the Mössbauer QS of $SnBr_4(OPPh_3)_2$. While the crystal structure corresponded to the trans isomer,[13] the QS (0.61 mm s^{-1})[14] 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*-$SnBr_4(OPPh_3)_2$ (0.89 mm s^{-1}), and the data for *cis*-$SnBr_4(OPPh_3)_2$, the relationship between the average Sn–Br distance (in Å) and the pqs of the ligands (in mm s^{-1}) for $SnBr_4L_2$ complexes is given by eq 1 (six points, $r = 0.996$).

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

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, bond distances, and bond angles (Tables S(1)–S(4)) (5 pages). Ordering information is given on any current masthead page.

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(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.[26]