Information from the Mössbauer Spectra of Tin(IV) Halide Complexes with 1,3-Diethylthiourea. A Redetermination of the Crystal Structure of Tetrachlorobis(1,3-diethylthiourea)tin(IV)‡

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The Mössbauer quadrupole splitting of octahedral tin(IV) chloride complexes can give information about the Sn–Cl bond lengths. As the value of *d*(Sn–Cl) reported previously for $SnCl_4(detu)_2$ (detu = 1,3-diethylthiourea) was too long for a complex showing a single line in the Mössbauer spectrum, we have redetermined the X-ray crystal structure, and found Sn–Cl distances which are compatible with the Mössbauer data. The compound crystallises in the centrosymmetric space group $R\bar{3}c$, and the structure is disordered about a crystallographic two-fold axis passing through Sn and two Cl atoms. The disorder does not allow the unambiguous distinction between a *cis* or *trans* structure by X-ray crystallography, but IR and Raman spectroscopies show that both $SnCl_4(detu)_2$, and the new compound $SnF_4(detu)_2$, have a *cis* geometry. The isomer shift values for $SnX_4(detu)_2$ are −0.04, 0.62, 0.96 and 1.21 mm s^{-1} for X = F, Cl, Br and I, respectively. The values for X = Cl and Br are much higher than previous values, and fully consistent with S-co-ordination by the detu ligand. The information on the donor atom in SnX_4L_2 complexes, which can sometimes be obtained from the Mössbauer isomer shift, is discussed.

We have reported recently that the Mössbauer quadrupole splitting (q.s.) can give quantitative as well as qualitative information about the structure of octahedral tin(IV) chloride complexes, as the average Sn–Cl distance is related to the partial quadrupole splitting (p.q.s.) of the ligands by means of equation (1), where 4 p.q.s. = −q.s. for *trans* compounds or 2 q.s. for *cis* compounds.[1] Equation (1) can be used to estimate

$$d(\text{Sn–Cl})/\text{Å} = (-0.044 \pm 0.002)(4\ \text{p.q.s.}) + (2.420 \pm 0.003) \quad (1)$$

Sn–Cl distances, which are expected to agree with experimental values within ±0.02 Å, and rationalises the experimental Sn–Cl distances and q.s. data reported in the literature in terms of the donor properties of the ligands. In the case of tetrachlorobis(1,3-diethylthiourea)tin(IV), however, the long average *d*(Sn–Cl) reported (2.53 Å)[2] was not compatible with equation (1) since a narrow single line was observed in the Mössbauer spectrum. The structure had been solved in the non-centrosymmetric space group *R*3*c* although $R\bar{3}c$ was quoted (the Cambridge Crystallographic Data Centre confirmed this error), and a wide crystalline disorder was reported, although the exact nature of the disorder was not noted.[2] The discrepancy between the published structure and the predictions from equation (1) prompted us to redetermine the crystal structure and Mössbauer data of $SnCl_4(detu)_2$ (detu = 1,3-diethylthiourea).

The ^{119}Sn Mössbauer isomer shift (i.s.) reflects the s electron density at the tin nucleus, and is sensitive to the electronegativities of the atoms bonded to tin. In agreement with this idea, it was noted that in the case of octahedral tin(IV) halide complexes, the i.s. varied with the donor atom in the general order O < N < S < P,[3] and a correlation table could be constructed.[4] In fact, the i.s. has been used to determine the donor atom in SnX_4 complexes with organic ligands.[5–7] In $SnX_4(detu)_2$ (X = Cl or Br),[2] the reported i.s. values (0.31 and 0.39 mm s^{-1}) seem to be rather low for a S-bonded ligand[4,6] and we have redetermined both values. In order to complete the series, we have also recorded the Mössbauer spectrum of $SnI_4(detu)_2$ and prepared and characterised $SnF_4(detu)_2$.

Experimental

Care was taken to exclude moisture during the preparation of the complexes. Compounds $SnX_4(detu)_2$ (X = Cl, Br or I) were prepared as reported previously,[2] using C_6H_6 and CH_2Cl_2 as solvents. The complexes gave satisfactory elemental analyses and melting points [literature values[2] in parentheses: 158–160 (155) for X = Cl, 139 (139) for X = Br and 137 (decomp.) (135 °C) for X = I]. Carbon, H and N microanalyses were carried out by the Microanalytical Service, Universidad Autónoma de Madrid and F and S microanalyses by Galbraith Laboratories, Inc., Knoxville, TN.

Infrared spectra were recorded on a Nicolet 5 DX FT-IR instrument in the range 4000–250 cm^{-1}, using Nujol mulls between CsI windows. Raman spectra were recorded on a Jarrell-Ash spectrophotometer, model 25-300, using a Kr^+ (6471 Å) laser. 119-Tin Mössbauer spectra were obtained on a Ranger Scientific Inc. MS-1200 constant-acceleration Mössbauer spectrometer. A standard source of $Ca^{119}SnO_3$ was used at room temperature in transmission geometry, and the polycrystalline samples were cooled to 80 K by means of a liquid nitrogen cryostat. Isomer shifts are relative to $BaSnO_3$ at room temperature, and the estimated error is ±0.05 mm s^{-1}. The Mössbauer spectrum of $SnBr_4(detu)_2$ was also obtained with use of the system and conditions described previously.[8] All the spectra displayed single lines with widths in the range 0.93–1.17 mm s^{-1}.

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Crystallographic results for $SnCl_4(detu)_2$ in the space groups $R3c$ and $R\bar{3}c$

	Space group	
	$R3c$	$R\bar{3}c$
R	0.037	0.028
R'	0.048	0.034
Parameters refined	190	161
ρ_{max}/e Å^{-3}	0.7	0.4
C(sp^2)–N/Å	1.28(2)–1.57(3)	1.287(11)–1.347(13)
N–C(sp^3)/Å	1.38(3)–1.86(4)	1.48(2)–1.59(2)
C–C/Å	0.84(4)–1.53(3)	1.31(3)–1.50(3)
N–C–N/°	105(1)–115(1)	116.7(8)–120.7(8)
C–N–C/°	107(2)–125(2)	123(1)–127(1)
N–C–C/°	71(2)–143(6)	108(1)–115(2)

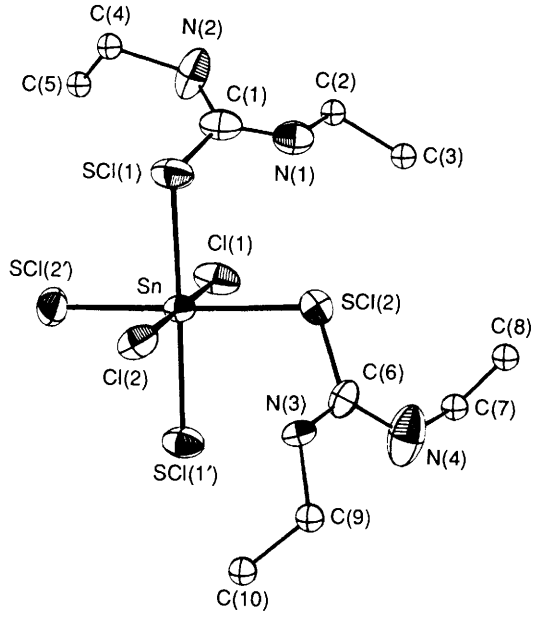

Fig. 1 ORTEP plot of $SnCl_4(detu)_2$. The structure is disordered about a two-fold axis passing through Cl(1), Sn and Cl(2). SCl are the disordered S and Cl atoms with 50/50 population. The organic parts bonded to SCl(1') and SCl(2') have been omitted for clarity and arbitrary thermal ellipsoids have been drawn for C(2)–C(5) and C(7)–C(10)

Synthesis of Bis(1,3-diethylthiourea)tetrafluorotin(IV).—The complex $SnF_4(MeCN)_2$[9] (0.70 g, 2.5 mmol) and detu (0.74 g, 5.6 mmol) were stirred at room temperature in tetrahydrofuran (thf) (40 cm^3) for 4 h. The resulting solid was filtered off, washed with thf and dried in air to yield $SnF_4(detu)_2$ (0.84 g, 72%) as a white powder, m.p. 181–184 (decomp.) °C (Found: C, 25.3; H, 5.1; F, 16.3; N, 11.6; S, 13.2. $C_{10}H_{24}F_4N_4S_2Sn$ requires C, 26.2; H, 5.3; F, 16.55; N, 12.2; S, 14.0%). IR (Nujol): 3250vs (br), 3170s [ν(NH)]; 1601vs, 1568vs [ν(CN)]; 800m [ν(CS)]; 542vs, 521vs, 504s and 449m [ν(SnF)] cm^{-1}. Mössbauer (80 K): i.s. = −0.04, Γ = 1.14 mm s^{-1}.

X-Ray Structure Determination of $SnCl_4(detu)_2$.—Yellow crystals were obtained by recrystallisation from CH_2Cl_2.

Crystal data. $C_{10}H_{24}Cl_4N_4S_2Sn$, M = 524.97, trigonal, space group $R\bar{3}c$, a = 18.392(3), c = 32.690(5) Å, U = 9576 Å^3 (by least-squares refinement on diffractometer angles for 24 automatically centred reflections, λ = 0.710 69 Å), T = 160(2) K, Z = 18, D_c = 1.639 g cm^{-3}, F(000) = 4716. Yellow prisms. Approximate crystal dimensions 0.2 × 0.2 × 0.3 mm, μ(Mo-Kα) = 17.55 cm^{-1}.

Data collection and processing.[10] CAD4 diffractometer, ω-2θ mode with ω scan width 0.75 + 0.35 tan θ, variable scan speed with maximum recording time 90 s, graphite-monochromated Mo-Kα radiation, T = 160(2) K; 3664 reflections measured ($1.5 \leqslant \theta \leqslant 25°$, h, k, $\pm l$), 1879 unique (merging R = 0.025), 1440 reflections with $I > 2\sigma(I)$ were considered as observed. The data were corrected for Lorentz and polarization effects, but not for absorption. No significant crystal decay was observed.

Structure analysis and refinement. The structure was first refined in the non-centrosymmetric space group $R3c$, starting from the positions reported in ref. 2. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one, overall, refined U_{iso}[= 0.17(2) Å^2]. Final R and R' values were 0.037 and 0.048; weighting scheme $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics.[10] Programs used and sources of scattering factor data are given in ref. 10. The resulting structure shows a *cis*-octahedral configuration with two shorter Sn-Cl distances [Sn–Cl(1) 2.430(3) and Sn–Cl(2) 2.428(2) Å] *trans* to each other, and two longer distances [Sn–Cl(3) 2.521(8) and Sn–Cl(4) 2.459(8) Å] *trans* to the S-bonded ligands. While Sn–Cl(1) and Sn–Cl(2) are in excellent agreement with the expectations from equation (1), Sn–Cl(4) and especially Sn–Cl(3) seem to be rather long. The variation in chemically equivalent distances is still larger for C=S [S(1)–C(1) 1.747(15) and S(2)–C(6) 1.866(13) Å] and other bond lengths in the organic ligands (see Table 1). In addition to the unreasonable molecular geometry, the coordinates of Sn, Cl(1) and Cl(2) are very close to a crystallographic two-fold axis (positions 18 e) in the centrosymmetric space group $R\bar{3}c$. For that reason, we also considered the higher symmetry model which implies that the ligands and the Cl atoms *trans* to them are disordered about a two-fold axis passing through Cl(1), Sn and Cl(2).

The structure was solved in the $R\bar{3}c$ space group by the heavy-atom method, and refined by full-matrix least squares, with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogens were included in the refinement in the idealised positions, with a common isotropic thermal parameter which refined to U = 0.14(1) Å^2. New atomic scattering factors for the disordered SCl atoms (average value between S and Cl) were used in the structure factor calculations. The refinement converged to R = 0.028 and R' = 0.034 for 1440 unique observed reflections. The final difference map was void of any features of chemical significance. The final atomic coordinates for the non-hydrogen atoms are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

A comparison of the crystallographic results for $SnCl_4(detu)_2$ in the space groups $R3c$ and $R\bar{3}c$ (Table 1) shows unambiguously that the results in the centrosymmetric space group are far more satisfactory. This is shown by the lower R and R' values obtained in the latter (in spite of the fact that 29 fewer parameters were refined), lower standard deviations and residual electron density, and a more reasonable molecular geometry. In the disordered structure of $SnCl_4(detu)_2$ (Fig. 1), the Sn atom and the Cl atoms *trans* to each other [Sn–Cl(1) 2.429(1), Sn–Cl(2) 2.427(1) Å] lie on a crystallographic two-fold axis, and are not disordered, while there is a structural disorder which randomly exchanges the positions of the other Cl atoms and the ligands, in such a way that for those positions an average of the Sn–Cl and Sn–S bond lengths is obtained [Sn–SCl(1) 2.494(1), Sn–SCl(2) 2.470(1) Å]. In the related complexes $SnCl_2Me_2$·2dmtu and $SnCl_2Ph_2$·2dmtu (dmtu = 1,3-dimethylthiourea),[11] the Sn–S distances are *ca.* 0.1 Å longer than the Sn–Cl bond lengths, and we can estimate that the disordered Sn–Cl distances are similar to those not affected by disorder. The average of the four Sn–Cl distances is probably *ca.* 2.43 Å, in excellent agreement with the observation of a single

Table 2 Fractional atomic coordinates for $SnCl_4(detu)_2$

Atom	*x*	*y*	*z*
Sn	0.247 67(2)	1.000 00(0)	0.250 00(0)
Cl(1)	0.379 76(8)	1.000 00(0)	0.250 00(0)
Cl(2)	0.115 69(8)	1.000 00(0)	0.250 00(0)
SCl(1)*	0.175 07(8)	0.843 67(7)	0.252 65(3)
SCl(2)*	0.242 07(7)	1.000 80(7)	0.325 47(3)
N(1)	0.297 2(4)	0.893 8(5)	0.335 4(2)
N(2)	0.377 9(6)	1.017 7(6)	0.369 5(3)
N(3)	0.050 7(5)	0.833 0(5)	0.203 0(2)
N(4)	0.091 3(6)	0.738 0(6)	0.189 2(4)
C(1)	0.312 0(6)	0.971 2(6)	0.344 8(2)
C(2)	0.355 8(9)	0.862 9(10)	0.345 0(6)
C(3)	0.334 3(13)	0.789 5(12)	0.317 4(7)
C(4)	0.403 8(11)	1.109 0(10)	0.385 6(7)
C(5)	0.465 9(19)	1.163 9(12)	0.363 0(7)
C(6)	0.095 7(4)	0.799 5(5)	0.211 7(2)
C(7)	0.146 5(12)	0.699 1(11)	0.192 3(6)
C(8)	0.124 6(15)	0.641 5(17)	0.221 6(6)
C(9)	−0.007 3(11)	0.806 2(10)	0.167 2(5)
C(10)	0.002 6(17)	0.874 6(14)	0.140 4(9)

* SCl are the disordered S and Cl atoms with 0.5 occupancy factors.

Table 3 Vibrational Sn–X stretching frequencies (cm^{-1}) for $SnX_4(detu)_2$ (X = F or Cl)

$SnF_4(detu)_2$		$SnCl_4(detu)_2$		
IR	Raman	IR	Raman	ν(SnF)/ν(SnCl)
542vs	537w	306(sh)	305(sh)	1.77
521vs	—	296vs	294s	1.77
504s	—	285(sh)	—	1.77
449m	452w	266m	266m	1.69

line in the Mössbauer spectrum, and *ca.* 0.1 Å shorter than that reported previously.[2] The fact that equation (1) allowed us to detect the incorrectness of the previous structure determination strongly supports the accuracy and validity of the *d*(Sn–Cl) *vs.* p.q.s. correlation.

We can account for the observed disorder by assuming that molecules in *cis* positions occupy their positions in the crystal lattice with two different orientations related by a crystallographic two-fold axis passing through Cl(1), Sn and Cl(2). Although this is the most likely explanation, the existing disorder does not allow us to exclude unambiguously the possibility of a *trans* structure. While a *cis* structure such as suggested by Fig. 1 would require a 0.5 occupancy factor for the disordered ligands and Cl atoms, this would not be necessarily the case for the alternative disorder involving *trans* molecules. Unfortunately, the electron density distribution in the disordered structure prevented a meaningful refinement of the occupancy factors which were thus fixed at 0.5. Mössbauer spectroscopy is of no use in assigning a *cis* or *trans* structure to $SnCl_4(detu)_2$, as both isomers should display a single line, according to equation (1), for complexes with average Sn–Cl distances of *ca.* 2.43 Å. Infrared and Raman spectroscopies, on the other hand, can give information about the stereochemistry of $SnCl_4(detu)_2$. According to group theory, four Sn–X stretching vibrations are both IR and Raman active for *cis*-SnX_4L_2 (C_{2v} symmetry) complexes, while only one IR and two Raman ν(SnX), with alternation of activities, are expected for the *trans* isomer (D_{4h} symmetry). The data in Table 3 show that both $SnF_4(detu)_2$ and $SnCl_4(detu)_2$ have a *cis* structure. The consistency of the assignments is supported by the ratio ν(SnF)/ν(SnCl) which for related compounds has an average value of 1.77 (standard deviation 0.04).[9] Furthermore, both the average ν(SnCl) and the $\nu_2(A_1)$ mode are fully consistent with the single line observed in the Mössbauer spectrum, according to the correlation reported previously with the q.s.[12] Two weak bands at 350 and 360 cm^{-1} had previously been assigned as ν(Sn–Cl) modes,[2] but bands at such high frequencies would only be expected for $SnCl_4$ complexes with very weak donor ligands, which should display resolved doublets in the Mössbauer spectrum.[12,13] We can see that the Mössbauer q.s. can be useful for band assignment in vibrational spectra. It is rather surprising that despite obtaining an X-ray crystal structure refined to $R = 0.028$, we have to rely on vibrational spectroscopy to confirm the *cis* structure for $SnCl_4(detu)_2$.

Mössbauer Isomer Shifts.—The i.s. of $SnCl_4L_2$ complexes is higher for S-bonded ligands than for N-bonded donors.[3–7] We have reviewed the reference bank of the Mössbauer Effect Data Centre (University of North Carolina, USA), and found that the average i.s. for 28 S-bonded octahedral $SnCl_4$ complexes is 0.66 mm s^{-1} (standard deviation 0.06 mm s^{-1}), while the average i.s. for 35 N-bonded $SnCl_4$ complexes is 0.42 mm s^{-1} (standard deviation 0.08 mm s^{-1}). In view of these ranges, the i.s. value of 0.31 mm s^{-1} reported for $SnCl_4(detu)_2$[2] seems to be rather low, since the X-ray structure determination has shown that the ligand co-ordinates through the S atom. Even more surprising is the i.s. value of 0.39 mm s^{-1} reported for $SnBr_4(detu)_2$,[2] since the i.s. of $SnBr_4$ complexes is *ca.* 0.27 mm s^{-1} (standard deviation 0.07 mm s^{-1}) higher than those of the corresponding $SnCl_4$ complexes.[9] We have measured the following i.s. values for $SnX_4(detu)_2$: −0.04 for X = F, 0.62 for X = Cl, 0.96 (average of two determinations with two different spectrometers: 0.93, 0.98) for X = Br and 1.21 mm s^{-1} for X = I. These values are fully consistent with a S-bonded ligand, and the differences in i.s. values for the different halides agree with expectations from the literature.[9] The potential information on the donor atom in SnX_4L_2 complexes that can be obtained from Mössbauer i.s. values is often neglected. For instance, one of us stated in 1982 that the i.s. value could not distinguish whether sulphur or nitrogen atoms were bonded to tin in $SnCl_4$-$(S_4N_4)_2$.[14] Nevertheless, the i.s. value of 0.45 mm s^{-1} would have been an indication of N-atom co-ordination as shown later by a single-crystal X-ray diffraction study.[15] For the related compound $[1,5\text{-}(Ph_2P)_2N_4S_2]_4 \cdot 3SnCl_4$,[16] a structure has been proposed with the tin atoms in a *trans*-$SnCl_4L_2$ environment with N-bonded ligands.[16] We however believe that the measured i.s. value of 0.73 mm s^{-1} is more consistent with S-co-ordination, or with five-co-ordination at the tin atom (an i.s. of 0.70 mm s^{-1} has been reported for $SnCl_4 \cdot NMe_3$[17]).

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