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A Mössbauer and Single-Crystal X-ray Structural Study of Hexa- and Pentacoordinate Organotin(IV) Compounds Containing Urea-Type Derivatives

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A number of hexa- and pentacoordinate diorganotin(IV) complexes of general formulae R_2SnCl_2·2L and R_2SnCl_2·L (R = Me or Ph; L = urea or thiourea-type ligand) together with Ph_3SnCl·tmtu (tmtu = tetramethylthiourea) have been prepared and characterized by infrared and by Mössbauer spectroscopy. The crystal structures of Me_2SnCl_2·2dmtu (dmtu = 1,3-dimethylthiourea), $C_8H_{22}N_4S_2Cl_2Sn$ (**1**), Ph_2SnCl_2·2dmtu, $C_{18}H_{26}N_4S_2Cl_2Sn$ (**2**), and Ph_3SnCl·tmu (tmu = tetramethylurea), $C_{23}H_{27}N_2OClSn$ (**3**), solved by X-ray analysis are reported. **1** and **2** crystallize in the monoclinic system of space group $P2_1/n$. **1**: $a = 9.843$ (3) Å, $b = 9.864$ (3) Å, $c = 9.089$ (3) Å, $\beta = 100.1$ (4)°, $Z = 2$. **2**: $a = 10.791$ (3) Å, $b = 11.468$ (4) Å, $c = 10.147$ (4) Å, $\beta = 93.9$ (3)°, $Z = 2$. Both compounds consist of discrete molecules with nearly regular trans-octahedral tin(IV) coordination and the following bond lengths: Sn–S = 2.729 (1) and 2.686 (2) Å, Sn–C = 2.122 (5) and 2.151 (7) Å, and Sn–Cl = 2.616 (1) and 2.589 (2) Å for **1** and **2**, respectively. **3** crystallizes in the orthorhombic system of space group *Pcab* (no. 61) with $a = 29.977$ (9) Å, $b = 14.235$ (5) Å, $c = 11.034$ (4) Å, and $Z = 8$. The lattice of **3** contains discrete molecules with tin having a distorted trigonal-bipyramidal geometry with the following bond lengths: $Sn–C_{eq} = 2.12$ (1), 2.15 (1), and 2.11 (1) Å, $Sn–Cl_{ap} = 2.485$ (4) Å, and $Sn–O_{ap} = 2.383$ (8) Å.

Introduction

Many tin(IV) complexes of type SnX_4·2L, X = Cl, Br, or I; L = urea or thiourea derivative, have been reported previously.[1] In those compounds a cis-octahedral coordination geometry around the tin(IV) center has been proposed on the basis of infrared and Mössbauer techniques and confirmed by X-ray studies on $SnBr_4$·2deu and $SnCl_4$·2detu.

The factors affecting the coordination site in inorganic and organotin(IV) compounds are now considered for new complexes of general formulae R_2SnCl_2·2L and R_nSnCl_{4-n}·L (n = 2, 3; R = Me, Ph; L = urea, 1,3-dimethylurea (dmu), 1,3-dimethylthiourea (dmtu), 1,3-diethylurea (deu), 1,3-diethylthiourea (detu), tetramethylurea (tmu), and tetramethylthiourea (tmtu)).

The crystal structures of Me_2SnCl_2·2dmtu, Ph_2SnCl_2·2dmtu, and Ph_3SnCl·tmu have been solved and together with Me_2SnCl_2·tmu, which we described in a preliminary communication,[2] are the only known compounds containing urea derivatives bonded to an organotin(IV) center.

Experimental Section

Preparation of Me_2SnCl_2·2urea and Me_2SnCl_2·2dmu. To a well-stirred solution of Me_2SnCl_2 (500 mg, 2.5 mmol) in ethanol (20 mL) was added, dropwise, a solution of the ligand (urea, 300 mg, 5 mmol; dmu, 400 mg, 5 mmol) in the same solvent, and the solution was stirred for a further hour. The white precipitate obtained on addition of pentane was collected by filtration, washed with small quantities of a mixture of ethanol and pentane, and dried under vacuum.

Preparation of Me_2SnCl_2·2dmtu. A solution of dmtu (520 mg, 5 mmol) in ethanol (30 mL) was added slowly to an ethanolic solution of Me_2SnCl_2 (500 mg, 2.5 mmol). The resulting solution was stirred for some hours, and the white precipitate obtained on addition of pentane was collected by filtration, washed, and dried under vacuum.

Preparation of Me_2SnCl_2·2detu. The ligand (660 mg, 5 mmol) was dissolved in CH_2Cl_2 (20 mL) and added dropwise to a solution of Me_2SnCl_2 (500 mg, 2.5 mmol) in the same solvent. The resulting solution was stirred for a short time, and the white solid was obtained on addition of cyclohexane, was filtered, washed with small quantities of the solvent, and dried under vacuum.

Preparation of Ph_2SnCl_2·2dmtu. A solution of the ligand (750 mg, 7.5 mmol) in acetone was added dropwise to a solution prepared by dissolving Ph_2SnCl_2 (650 mg, 2.5 mmol) in acetone (20 mL). The white solid which was formed slowly on addition of diethyl ether (about 30 mL), was collected by filtration, washed, and dried under vacuum.

Preparation of Ph_2SnCl_2·2deu and Ph_2SnCl_2·2detu. A 5-mmol solution of the appropriate ligand in methyl ethyl ketone (about 30 mL) was added dropwise to a well-stirred solution of Ph_2SnCl_2 (650 mg, 2.5 mmol) in the same solvent. Further stirring of the resulting solution results in the slow precipitation of a white solid that was filtered, washed with the solvent, and dried under vacuum.

Preparation of Ph_2SnCl_2·2tmu. The ligand (580 mg, 5 mmol) was added directly to a solution of Ph_2SnCl_2 (650 mg, 2.5 mmol) in methyl ethyl ketone. A white solid was formed slowly by stirring the solution, collected by filtration, washed with the solvent, and dried under vacuum.

Preparation of Me_2SnCl_2·tmu. Me_2SnCl_2 (500 mg, 2.5 mmol) was dissolved in methyl ethyl ketone, and to this solution was added the pure ligand (0.28 mL, 2.5 mmol) dropwise. The white solid obtained on addition of pentane was filtered, washed with the solvent and dried under vacuum.

Preparation of Me_2SnCl_2·tmtu. Me_2SnCl_2 (500 mg, 2.5 mmol) and the ligand (330 mg, 2.5 mmol) were dissolved in methyl ethyl ketone (about 20 mL) and the two solutions mixed slowly. Pentane was added to the resulting solution, and the pale green oil obtained was decanted and the supernatant liquid poured off. The white solid product was obtained when the oil was kept in a desiccator over P_4O_{10}.

Preparation of Ph_2SnCl_2·tmtu. tmtu (330 mg, 2.5 mmol) was dissolved in acetone and the solution poured dropwise into

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[1] Calogero, S.; Russo, U.; Barnard, P. W. C.; Donaldson, J. D. *Inorg. Chim. Acta* **1982**, *59*, 111.

[2] Calogero, S.; Valle, G.; Russo, U. *J. Organomet. Chem.* **1982**, *228*, C79.

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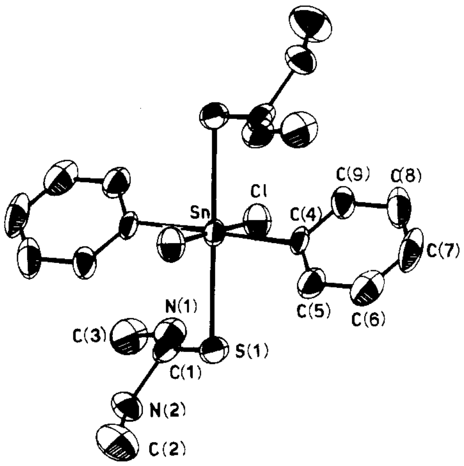

Figure 1. ORTEP plot of $Me_2SnCl_2 \cdot 2dmtu$.

a solution of Ph_2SnCl_2 (650 mg, 2.5 mmol) in the same solvent. The addition of petroleum ether resulted in the formation of a light yellow oil and a colorless supernatant liquid that was poured off. The oil solidified under vacuum to give the white powder.

Preparation of $Ph_3SnCl \cdot tmu$. Ph_3SnCl (950 mg, 2.5 mmol) was dissolved in diethyl ether, and pure tmu (0.28 mL, 2.5 mmol) was added dropwise. The solvent was evaporated, and the white crystalline product obtained filtered, washed, and dried under vaccum.

All the complexes were washed with small quantities of the solvent, dried under vacuum, and recrystallized until constant analysis. The compounds are all stable in the open area, and their yields are generally moderate to high (70–90%). All chemical were purchased from commercial sources and either used as received or purified. The infrared spectra were recorded on a Perkin-Elmer 580 B spectrophotometer in KBr pellets and Nujol mulls. Analytical data are reported in Table I together with the most relevant infrared data. Mössbauer spectra were obtained by using equipment and procedures reported previously.[1]

Crystallographic Analyses. The crystallographic data are listed in Table II. Intensity data were collected in an air-conditioned room, 22 ± 1 °C, on a four-circle Philips PW 1100 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) in the range $2 < \theta < 25°$ by using the 2–2θ scan mode. Lorentz and polarization corrections were applied. The systematic absences for $h0l$, $h + l = 2n + 1$, and for $0k0$, $k = 2n + 1$, are indicative of the space group $P2_1/n$ for $Me_2SnCl_2 \cdot 2dmtu$ or $Ph_2SnCl_2 \cdot 2dmtu$. The systematic absences for $hk0$, $k = 2n + 1$, for $h0l$, $h = 2n + 1$, and $0kl$, $l = 2n + 1$, are indicative of the space group $Pcab$ for $Ph_3SnCl \cdot tmu$.

The structures were solved by using three-dimensional Patterson and Fourier syntheses; a least-squares refinement on F was computed. The unitary weighting scheme was used because it presented the best convergence. The SHELX 76 program was used.[3] All the non-hydrogen atoms were refined anisotropically; the positions of the hydrogen atoms were located from a difference Fourier map, but only those in $Me_2SnCl_2 \cdot 2dmtu$ were isotropically refined. The final atomic coordinates are reported in Tables III and IV the bond distances and angles in Table V and VI. The ORTEP diagrams[4] of the molecular structure for $Me_2SnCl_2 \cdot 2dmtu$, $Ph_2SnCl_2 \cdot 2dmtu$, and $Ph_3SnCl \cdot tmu$, showing the atomic labeling scheme are in Figures 1, 2, and 3, respectively.

Results and Discussion

Crystal Structures. The crystal structures of both $Me_2SnCl_2 \cdot 2dmtu$ (Figure 1) and $Ph_2SnCl_2 \cdot 2dmtu$ (Figure 2) consist of discrete covalent molecules. In both compounds the tin(IV) atoms are in special position ($\bar{1}$) and have trans-octahedral coordination geometry. The tin(IV) coordination polyhedron has Sn bonded to two S atoms from the dmtu ligands, two chlorine atoms, and two carbon atoms at distances of 2.729, 2.616, and 2.122 Å, respectively, in $Me_2SnCl_2 \cdot 2dmtu$ and of 2.686, 2.589, and 2.151 Å, respectively, in $Ph_2SnCl_2 \cdot 2dmtu$.

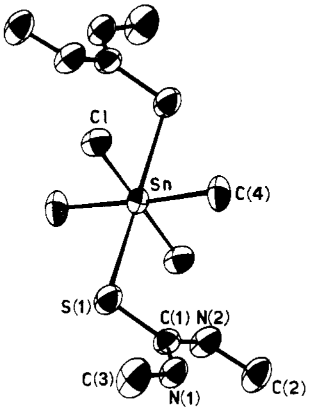

Figure 2. ORTEP plot of $Ph_2SnCl_2 \cdot 2dmtu$.

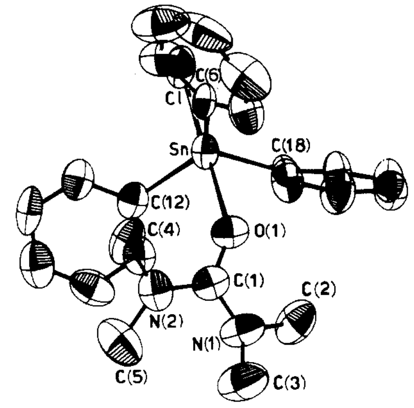

Figure 3. ORTEP plot of $Ph_3SnCl \cdot tmu$.

The tin(IV) coordination geometry is nearly regular in both compounds. The data in Table V show that there are small deviations from the ideal geometry in the C–Sn–Cl, S–Sn–C, and S–Sn–Cl bond angles of −0.5, +2.8, and −2.5°, respectively, in the dimethyl derivative and of −0.9, +2.5, and +0.8°, respectively, in the diphenyl compound.

The ligand coordination through the sulfur atom in $R_2SnCl_2 \cdot 2dmtu$, R = Me or Ph, shown by X-ray analyses, may be extended to all the homologous compounds in Table I because the shift of the ν(CS) or ν(CO) frequency is negative, while the one of the ν(CN) is positive on going from the free to the coordinate ligand. As a consequence of the coordination, there is a decrease in double-bond character of the thioketo or keto group with an increase in the CN bond order.

The infrared data for all the $R_2SnCl_2 \cdot 2L$ complexes are also consistent with an all-trans geometry around the tin(IV) atom because only the asymmetric stretchings Sn–C and Sn–Cl are found at about 580 or 290 cm^{-1} and 240 cm^{-1}, respectively. However it is not possible to rule out the presence of the symmetric ν(Sn–C) because of bands due to the ligands present in the same region. In any case it is worthwhile to point out also that the ν_{as}(Sn–C) bands of all the Me_2SnCl_2 complexes are broad, while they are sharp and symmetric for the Ph_2SnCl_2 derivatives that have ν_{as}(Sn–Cl) about 10 cm^{-1} lower than in the dimethyl complexes.

The possible hydrogen bonds S(1)···HN(1) are at distances of 2.76 Å in $Me_2SnCl_2 \cdot 2dmtu$ and of 2.40 Å in $Ph_2SnCl_2 \cdot 2dmtu$.

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[3] Sheldrick, G. M. SHELX 76, System of Computing Programs, University of Cambridge, England, 1976.

[4] Johnson, C. K. ORTEP, Report ORNL-3794, Oak Ridge, Tenn., 1965.

Table I. Analytical Data

	mp[a]	anal. found[b] C	H	N	Cl	$\Delta\nu$(CO)/ $\Delta\nu$(CS)[c]	$\Delta\nu$(CN)[d]	ν_{as}(Sn–C)[d]	ν_{as}(Sn–Cl)[d]
Me$_2$SnCl$_2$·2urea	87	13.8 (14.1)	4.1 (4.1)	17.3 (16.5)	21.5 (20.9)	−38	+44	584 m, br	244 s
Me$_2$SnCl$_2$·2dmu		24.0 (24.3)	5.6 (5.6)	13.8 (14.1)	17.4 (17.9)	−20	+30	581 m, br	240 s
Me$_2$SnCl$_2$·2dmtu	103	23.2 (22.5)	5.2 (5.2)	13.2 (13.1)	16.0 (16.6)	−8	+12	573 m, br	246 s
Me$_2$SnCl$_2$·2detu	48	28.3 (29.8)	6.0 (6.2)	10.9 (11.6)	15.0 (14.6)	−10	+8	585 m, br	242 s
Ph$_2$SnCl$_2$·2dmtu	108	38.9 (39.2)	4.9 (4.7)	10.2 (10.1)	12.3 (12.8)	−28	+10	287 s	231 s
Ph$_2$SnCl$_2$·2deu	144	44.8 (45.9)	6.3 (5.9)	9.4 (9.7)	12.8 (12.3)	−22	+49	292 s	225 s
Ph$_2$SnCl$_2$·2detu	144	42.8 (43.6)	5.7 (5.6)	9.2 (9.2)	12.1 (11.7)	−53	+9	287 s	229 s
Ph$_2$SnCl$_2$·2tmu	92	44.9 (45.9)	5.7 (5.9)	9.8 (9.7)	12.4 (12.3)	−28	+41	293 s	230 m
Me$_2$SnCl$_2$·tmu	65	25.0 (25.0)	5.5 (5.4)	8.4 (8.3)	21.2 (21.1)	−90	+36	568 m (518 w)	324 s, br (244 s)
Me$_2$SnCl$_2$·tmtu	57	23.8 (23.9)	5.1 (5.2)	8.0 (8.0)	19.9 (20.2)	−6	+75	557 m (517 m)	323 s (241 s, br)
Ph$_2$SnCl$_2$·tmtu	112	42.2 (42.9)	4.6 (4.7)	6.0 (5.9)	14.5 (14.9)	−38	+78	297 sh (236 s, br)	317 s (275 s)
Ph$_3$SnCl·tmu		55.7 (55.1)	5.5 (5.4)	5.6 (5.6)	6.9 (7.1)	−39	+48		

[a] Melting points, in °C, were determined under vacuum and are uncorrected. [b] Calculated values are in parentheses. [c] In cm^{-1} from the uncoordinated ligand. [d] The symmetric frequencies are in parentheses.

The coordination geometries of the compounds R$_2$SnCl$_2$·L (Table I) can be deduced from the crystal structures of Ph$_3$SnCl·tmu (Figure 3) and Me$_2$SnCl$_2$·tmu[2] which consist of discrete covalent molecules with trigonal-bipyramidal geometry around the tin(IV) center. The apical positions of these polyhedra are occupied by the more electronegative ligands, the tmu oxygen, and one chlorine atom so that Ph$_3$SnCl·tmu has cis and Me$_2$SnCl$_2$·tmu trans-equatorial trigonal-bipyramidal geometry. The apical Sn–Cl bond length in Me$_2$SnCl$_2$·tmu is 0.125 Å longer than the equatorial one, probably as a consequence of the different steric angles between the equatorial and the apical ligands.[5]

The ligand coordination through the oxygen atom in Ph$_3$SnCl·tmu and Me$_2$SnCl$_2$·tmu, or through the sulfur atom in Me$_2$SnCl·tmtu and Ph$_2$SnCl$_2$·tmtu, is consistent with the infrared frequency shifts in Table I. All the pentacoordinate complexes have both the symmetric and the asymmetric SnC and SnCl stretching bands. These bands suggest a cis arrangement for the methyl or phenyl groups and for the chlorine atoms.

The angular distortion in the equatorial plane of Me$_2$SnCl$_1$·tmu is much greater than in Ph$_3$SnCl·tmu, probably due to the absence in this plane of the strongly electronegative chlorine atom (Table VI). The O–Sn–Cl apical angle is nearly 180° in both compounds. The tin(IV) atoms in Ph$_3$SnCl·tmu and Me$_2$SnCl$_2$·tmu are displaced from the least-squares equatorial planes toward the apical chlorine atoms by 0.16 and 0.15 Å, respectively (see Table VII, available as supplementary material. The positions of the S(1), C(1), N(1), and N(2) atoms that define the thiourea planes in Table VII for R$_2$SnCl$_2$·2dmtu show that the dmtu skeletons are planar. The tmu skeleton is also planar both in Ph$_3$SnCl·tmu and Me$_2$SnCl$_2$·tmu. The equatorial and the phenyl planes in Ph$_3$SnCl·tmu determine the dihedral angles given in Table VII probably because of steric hindrance. The widest dihedral angle, 49.2°, corresponds to the phenyl ring with the longest bond length Sn–C (12). Steric hindrance also determines the large Sn···Sn distances in Ph$_3$SnCl·tmu, 7.7 Å, in comparison with 4.7 Å in Me$_2$SnCl$_2$·tmu.

Mössbauer Parameters. The Mössbauer spectra of the compounds in Table VIII are characterized by a large electric quadrupole splitting ΔE_Q, and by a relatively high isomer shift, S. Line widths, $2\Gamma_{av}$, between 0.90 and 1.12 mm/s were obtained with a Ca^{119m}SnO$_3$ source and absorbers containing about 0.5 mg of ^{119}Sn/cm^2. For the compounds in Table VIII the s electron density at the tin nucleus, the electric quadrupole coupling, and the line width show the usual trend in the range 78–200 K. The temperature decrease of the recoil-free fraction generally determines an undetectable effect above 200 K.

The isomer shift becomes more negative on going from the methyl to the phenyl analogues or on going from the thiourea-type to the urea-type analogues and reachs a minimum for Ph$_3$SnCl·tmu.

The quadrupole coupling at the tin nucleus is largely generated from an electron unbalance among the differently occupied p orbitals because of σ bonding, coordination geometry, and deviations from the ideal values. The tin coordination geometry, in particular, may be investigated on a semiquantitative basis by the additive model. With this aim, the following partial quadrupole splitting

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(5) (a) Zahrobsky, R. F. *J. Am. Chem. Soc.* 1971, *93*, 3313. (b) One of the reviewers suggests that the reason for the longer central atom–ligand bonds relative to the equatorial bond containing the same ligand is that the orbital description provides a weaker axial bond in a trigonal bipyramid.

Table II. Crystallographic Data

	$Me_2SnCl_2 \cdot 2dmtu$	$Ph_2SnCl_2 \cdot 2dmtu$	$Me_2SnCl_2 \cdot tmu$[a]	$Ph_3SnCl \cdot tmu$
unit cell	monoclinic	monoclinic	monoclinic	orthorhombic
formula	$C_8H_{22}N_4S_2Cl_2Sn$	$C_{18}H_{26}N_4S_2Cl_2Sn$	$C_7H_{18}N_2OCl_2Sn$	$C_{23}H_{27}N_2OClSn$
fw, amu	428.01	552.15	335.83	601.63
space group	$P2_1/n$	$P2_1/n$	$P2_1/2$	*Pcab* (no. 61)
a, Å	9.843 (3)	10.791 (3)	16.241 (9)	29.977 (9)
b, Å	9.864 (3)	11.468 (4)	9.624 (6)	14.235 (5)
c, Å	9.089 (3)	10.147 (4)	8.659 (5)	11.034 (4)
β, deg	100.1 (4)	93.9 (3)	96.8 (3)	
V, Å^3	868.9 (5)	1252.8 (6)	1344.0 (6)	4708.5 (1)
Z	2	2	4	8
d_{obsd}, g/cm^3	1.62 (3)	1.45 (2)	1.64 (3)	1.40 (2)
d_{calcd}, g/cm^3	1.64 (3)	1.46 (4)	1.66 (3)	1.41 (3)
cryst dimens, mm	0.20 × 0.20 × 0.30	0.40 × 0.30 × 0.20	0.25 × 0.20 × 0.40	0.20 × 0.40 × 0.40
F(000)	428	556	664	2032
no. of reflctns measd	1732	1499	2687	3283
data used, $I > 3\sigma(I)$	1369	1424	2036	2125
R	0.026	0.045	0.038	0.058
μ, cm^{-1}	20.53	13.01		11.08

[a] From ref. 2

Table III. Final Atomic Coordinates for $Ph_2SnCl_2 \cdot 2dmtu$ and $Me_2SnCl_2 \cdot 2dmtu$ with Esd's in Parentheses

	$Ph_2SnCl_2 \cdot 2dmtu$			$Me_2SnCl_2 \cdot 2dmtu$		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Sn[a]	0.0	0.0	0.0	0.0	0.0	0.0
Cl	0.2187 (2)	−0.0865 (2)	−0.0250 (2)	0.2246 (1)	−0.1142 (2)	0.1430 (2)
S(1)	0.0411 (2)	0.0037 (3)	0.2640 (2)	0.0996 (2)	−0.0451 (2)	0.7423 (2)
N(1)	0.1635 (7)	0.1795 (7)	0.3884 (7)	0.1981 (6)	0.1306 (6)	0.5674 (6)
N(2)	0.2645 (7)	0.0905 (7)	0.2255 (7)	0.0046 (5)	0.1989 (6)	0.6515 (6)
C(1)	0.1641 (8)	0.0978 (8)	0.2961 (7)	0.1013 (6)	0.1066 (6)	0.6461 (6)
C(2)	0.3652 (10)	0.1736 (10)	0.2330 (11)	−0.0020 (8)	0.3290 (7)	0.5763 (9)
C(3)	0.0530 (12)	0.2002 (11)	0.4667 (11)	0.3077 (10)	0.0362 (9)	0.5468 (12)
C(4)	0.0761 (7)	0.1719 (6)	−0.0206 (8)	0.0976 (7)	0.1921 (6)	0.0340 (8)
C(5)	0.0406 (9)	0.2599 (7)	0.0630 (9)			
C(6)	0.0912 (11)	0.3710 (8)	0.0501 (12)			
C(7)	0.1733 (12)	0.3948 (9)	−0.0451 (14)			
C(8)	0.2056 (10)	0.3077 (10)	−0.1290 (11)			
C(9)	0.1579 (9)	0.1940 (8)	−0.1156 (9)			

[a] Occupancy 0.5.

Table IV. Final Atomic Coordinates for $Ph_3SnCl \cdot tmu$ with Esd's in Parentheses

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Sn	0.1192 (0)	0.5814 (1)	0.3873 (1)	C(10)	0.2030 (6)	0.4644 (10)	0.0986 (14)
Cl	0.1400 (1)	0.4790 (3)	0.5607 (4)	C(11)	0.1676 (4)	0.4966 (9)	0.1673 (14)
O(1)	0.0981 (3)	0.6789 (5)	0.2213 (8)	C(12)	0.1208 (4)	0.7090 (9)	0.4915 (11)
N(1)	0.1541 (4)	0.7297 (7)	0.0962 (11)	C(13)	0.0884 (5)	0.7757 (10)	0.4725 (15)
N(2)	0.0864 (4)	0.6756 (7)	0.0187 (10)	C(14)	0.0898 (7)	0.8604 (11)	0.5443 (20)
C(1)	0.1117 (4)	0.6939 (7)	0.1150 (14)	C(15)	0.1237 (9)	0.8674 (16)	0.6338 (18)
C(2)	0.1772 (5)	0.7723 (9)	0.1969 (16)	C(16)	0.1561 (9)	0.7963 (18)	0.6483 (18)
C(3)	0.1804 (7)	0.7103 (13)	−0.0127 (19)	C(17)	0.1544 (6)	0.7175 (11)	0.5777 (13)
C(4)	0.0459 (5)	0.6185 (11)	0.0387 (16)	C(18)	0.0575 (4)	0.5148 (8)	0.3519 (11)
C(5)	0.0848 (7)	0.7348 (14)	−0.0873 (16)	C(19)	0.0173 (4)	0.5628 (8)	0.3524 (12)
C(6)	0.1737 (4)	0.5358 (8)	0.2806 (13)	C(20)	−0.0223 (4)	0.5188 (11)	0.3382 (14)
C(7)	0.2164 (5)	0.5404 (9)	0.3214 (13)	C(21)	−0.0243 (5)	0.4225 (13)	0.3172 (14)
C(8)	0.2529 (4)	0.5094 (10)	0.2541 (18)	C(22)	0.0165 (4)	0.3712 (9)	0.3111 (13)
C(9)	0.2456 (6)	0.4706 (10)	0.1431 (18)	C(23)	0.0555 (4)	0.4180 (8)	0.3313 (13)

values (pqs) were employed for Cl, Me, and Ph ligands belonging to an octahedral tin(IV) coordination site (0.0, −1.03, and −0.95 mm/s)[6] or to an apical trigonal-bipyramidal position (0.0, −0.94, and −0.89 mm/s).[7] The octahedral pqs value for $^1/_2(S_2CNEt_2)$ and for dimethyl sulfoxide (−0.25 and 0.01 mm/s)[8] were respectively assigned to the unreported pqs for the octahedral or apical trigonal-bipyramidal thioureic and ureic ligands. The relationship $3|L|^{tbe} - 4|L|^{tba} = 0.58$ mm/s[7] was used to connect the equatorial (tbe) and the apical (tba) trigonal-bipyramidal pqs values of the generic ligand L. The quadrupole splitting and the asymmetry parameter values, η, calculated by the usual point–charge model,[9] are reported in

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[6] Bancroft, G. M.; Platt, R. H. *Adv. Inorg. Radiochem.* **1972**, *15*, 59. Clark, M. G.; Maddock, A. G.; Platt, R. H. *J. Chem. Soc., Dalton Trans.* **1972**, 281.

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[9] The following expressions for the components of the electric field gradient tensor were used. (a) The trans-octahedral series $R_2SnCl_2 \cdot 2L$: $V_{xx}/e = 4|L| - 2|R| - 2|Cl|$; $V_{yy}/e = 4|R| - 2|L| - 2|Cl|$; $V_{zz}/e = 4|Cl| - 2|L| - 2|R|$. (b) The cis-trigonal-bipyramidal series $R_2SnCl_2 \cdot L$: $V_{xx}/e = 2|Cl|^{tbe} - {}^1/_2|R|^{tbe} - |Cl|^{tba} - |L|^{tba}$; $V_{yy}/e = -|Cl|^{tbe} + {}^5/_2|R|^{tbe} - |Cl|^{tba} - |L|^{tba}$; $V_{zz}/e = -|Cl|^{tbe} - 2|R|^{tbe} + 2|Cl|^{tba} + 2|L|^{tba}$. (c) The equatorial trigonal-bipyramidal $Ph_3SnCl \cdot tmu$: $V_{xx}/e = V_{yy}/e = {}^3/_2|Ph|^{tbe} - |Cl|^{tba} - |tmu|^{tba}$; $V_{zz}/e = -3|Ph|^{tbe} + 2|Cl|^{tba} + 2|tmu|^{tba}$. The principal axes *x*, *y*, and *z* are chose such that the ordering $|V_{xx}| \le |V_{yy}| \le |V_{zz}|$ holds. The asymmetry parameter and the quadrupole splitting values are calculated by using $\eta = (V_{xx} - V_{yy})/V_{zz}$ and $\Delta E_Q = {}^1/_2 e^2qQ(1 + \eta^2/_3)^{1/2}$.

Table V. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses

	$Me_2SnCl_2\cdot$ 2dmtu	$Ph_2SnCl_2\cdot$ 2dmtu
Sn–Cl	2.616 (1)	2.589 (2)
Sn–C(4)	2.122 (5)	2.151 (7)
Sn–S(1)	2.729 (1)	2.686 (2)
S(1)–C(1)	1.735 (5)	1.724 (8)
C(1)–N(1)	1.309 (6)	1.32 (1)
N(1)–C(3)	1.461 (8)	1.50 (1)
C(1)–N(2)	1.325 (6)	1.34 (1)
N(2)–C(2)	1.450 (7)	1.44 (1)
C(4)–C(5)		1.39 (1)
C(5)–C(6)		1.40 (1)
C(6)–C(7)		1.38 (2)
C(7)–C(8)		1.37 (2)
C(8)–C(9)		1.41 (1)
C(9)–C(4)		1.37 (1)
Cl–Sn–C(4)	89.5 (2)	89.1 (2)
S(1)–Sn–C(4)	92.8 (2)	92.5 (2)
S(1)–Sn–Cl	87.5 (1)	90.8 (1)
Sn–S(1)–C(1)	109.2 (2)	105.7 (2)
Sn–C(4)–C(5)		118.9 (6)
Sn–C(4)–C(9)		120.3 (6)
S(1)–C(1)–N(1)	120.2 (4)	122.4 (7)
S(1)–C(1)–N(2)	120.3 (4)	120.0 (7)
C(1)–N(1)–C(3)	125.4 (5)	122.0 (8)
C(1)–N(2)–C(2)	124.3 (4)	124.3 (8)
N(1)–C(1)–N(2)	119.5 (5)	117.7 (8)
C(4)–C(5)–C(6)		119 (1)
C(5)–C(6)–C(7)		121 (1)
C(6)–C(7)–C(8)		119 (1)
C(7)–C(8)–C(9)		120 (1)
C(8)–C(9)–C(4)		120 (1)
C(9)–C(4)–C(5)		121 (1)

parentheses in Table VIII.

Within the limits of the point-charge model and of the approximation used for some pqs values, the following predictions may be made: 1. compounds 1–8 of the series $R_2SnCl_2\cdot 2L$ have a trans-octahedral geometry with the chlorine atoms occupying the apical positions. This assignment agrees with the present structural data for $Me_2SnCl_2\cdot$2dmtu and $Ph_2SnCl_2\cdot$2dmtu; 2. compounds 9–11 of the series $R_2SnCl_2\cdot L$ have a cis-trigonal bipyramidal geometry with one chlorine atom and the urea-type derivative occupying the apical positions in agreement with the crystal structure of $Me_2SnCl_2\cdot$tmu;[2] 3. the compound $Ph_3SnCl\cdot$tmu has a trigonal-bipyramidal geometry with the phenyl groups occupying the equatorial positions as found in its crystal structure; 4. other possible isomers for the compounds of Table VIII are unacceptable because their calculated quadrupole splittings are not consistent with the observed data; 5. a positive sign may be assigned to the observed electric quadrupole coupling (Table VIII) except that for $Ph_3SnCl\cdot$tmu which is negative.

It is interesting to stress that while the organotin compounds of the $R_2SnCl_2\cdot 2L$ series (Table VIII) have a trans-octahedral geometry, the more similar compounds, i.e., the inorganic series $SnX_4\cdot 2L$ of Table IX, are, on the other hand, characterized by a cis-octahedral coordination. The presence of the trans-octahedral geometry in the organotin compounds 1–8 probably avoids the repulsive interactions that would exist among adjacent ligands whose steric angles superimpose each other in a cis configuration.[5] The cis-octahedral tin coordination geometry is, on the contrary, uninfluenced by the presence of branched ligands.[1]

On comparing the Mössbauer results for the trans-octahedral organotin and the cis-octahedral inorganic tin series (Tables VIII and IX), the most striking fact is the dramatic decrease of the quadrupole interaction.[10]

Table VI. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for $Me_2SnCl_2\cdot$tmu and $Ph_3SnCl\cdot$tmu

	$Me_2SnCl_2\cdot$ tmu[a]	$Ph_3SnCl\cdot$ tmu
Sn–Cl(1)	2.372 (2)	
Sn–Cl(2)	2.497 (2)	
Sn–Cl		2.485 (4)
Sn–O(1)	2.357 (4)	2.383 (8)
Sn–C(6)	2.100 (7)	2.12 (1)
Sn–C(7)	2.107 (7)	
Sn–C(12)		2.15 (1)
Sn–C(18)		2.11 (1)
$(C_{Ph}\text{–}C_{Ph})_{av}$		1.39 (4)
O(1)–C(1)	1.269 (7)	1.26 (2)
C(1)–N(1)	1.335 (8)	1.38 (2)
N(1)–C(2)	1.465 (9)	1.44 (2)
N(1)–C(3)	1.479 (9)	1.46 (2)
C(1)–N(2)	1.356 (8)	1.33 (2)
N(2)–C(4)	1.47 (1)	1.48 (2)
N(2)–C(5)	1.45 (1)	1.44 (2)
Cl(1)–Sn–Cl(2)	94.4 (1)	
Cl(1)–Sn–C(6)	104.5 (3)	
O(1)–Sn–C(6)	83.3 (3)	87.5 (4)
O(1)–Sn–C(7)	86.7 (3)	
O(1)–Sn–C(12)		85.7 (4)
O(1)–Sn–C(18)		83.5 (4)
O(1)–Sn–Cl		179.2 (2)
O(1)–Sn–Cl(1)	89.4 (1)	
O(1)–Sn–Cl(2)	176.2 (1)	
Cl(1)–Sn–C(7)	107.2 (3)	
Cl(2)–Sn–C(6)	95.2 (2)	
Cl(2)–Sn–C(7)	92.7 (2)	
Cl–Sn–C(6)		93.1 (4)
Cl–Sn–C(12)		94.5 (3)
Cl–Sn–C(18)		95.7 (3)
C(6)–Sn–C(7)	146.6 (3)	
C(6)–Sn–C(12)		122.6 (5)
C(6)–Sn–C(18)		115.9 (5)
C(12)–Sn–C(18)		119.8 (4)
$(Sn\text{–}C_{Ph}\text{–}C_{Ph})_{av}$		120 (1)
$(C_{Ph}\text{–}C_{Ph}\text{–}C_{Ph})_{av}$		120 (2)
Sn–O(1)–C(1)	132.6 (4)	136.8 (8)
O(1)–C(1)–N(1)	119.6 (6)	120 (1)
O(1)–C(1)–N(2)	120.8 (4)	122 (1)
C(1)–N(1)–C(2)	123.5 (6)	118 (1)
C(1)–N(1)–C(3)	117.7 (6)	123 (1)
C(2)–N(1)–C(3)	115.6 (6)	117 (1)
N(1)–C(1)–N(2)	119.6 (6)	118 (1)
C(1)–N(2)–C(4)	123.4 (7)	117 (1)
C(1)–N(2)–C(5)	120.1 (6)	124 (1)
C(4)–N(2)–C(5)	114.8 (7)	114 (1)

[a] From reference 2.

Table VIII. Mössbauer Parameters for Octahedral and Trigonal-Bipyramidal Organotin(IV) Compounds Containing Urea-type Derivatives at 78 K

		$\delta^{a,b}$	$\Delta E_Q{}^{a,c}$
1	$Me_2SnCl_2\cdot$2urea	1.32	4.49 (+4.18, 0.23)
2	$Me_2SnCl_2\cdot$2dmu	1.30	4.25 (+4.18, 0.23)
3	$Me_2SnCl_2\cdot$2dmtu	1.60	4.09 (+3.72, 0.41)
4	$Me_2SnCl_2\cdot$2detu	1.18	3.89 (+3.72, 0.41)
5	$Ph_2SnCl_2\cdot$2dmtu	1.48	3.40 (+3.41, 0.45)
6	$Ph_2SnCl_2\cdot$2deu	1.20	3.71 (+3.82, 0.02)
7	$Ph_2SnCl_2\cdot$2detu	1.12	3.50 (+3.41, 0.45)
8	$Ph_2SnCl_2\cdot$2tmu	1.25	3.60 (+3.82, 0.02)
9	$Me_2SnCl_2\cdot$tmu	1.13	3.71 (+3.10, 0.37)
10	$Me_2SnCl_2\cdot$tmtu	1.31	3.01 (+2.78, 0.13)
11	$Ph_2SnCl_2\cdot$tmtu	1.30	2.64 (+2.40, 0.05)
12	$Ph_3SnCl\cdot$tmu	1.02	2.86 (−2.96, 0.0)

[a] In mm/s; ±0.03 mm/s. [b] Relative to SnO_2. [c] The values calculated by the point-charge model are in parentheses (ΔE_Q, η).

The observation of unsplit or lightly split spectra in Table IX might appear astonishing because of the large

Table IX. Mössbauer Parameters for Cis-Octahedral Inorganic Tin(IV) Compounds Containing Urea-Type Derivatives at 78 K

	$S^{a,b}$	$\Delta E_Q{}^a$
$SnCl_4\cdot 2deu$	0.43	0.36
$SnCl_4\cdot 2tmu$	0.41	0.83
$SnBr_4\cdot 2dmu$	0.69	0.83
$SnBr_4\cdot 2tmu$	0.77	0.80
$SnCl_4\cdot 2detu^c$	0.31	0.0
$SnBr_4\cdot 2dmtu^c$	0.40	0.0
$SnBr_4\cdot 2detu^c$	0.39	0.0

[a] In mm/s; ±0.04 mm/s. [b] Relative to SnO_2. [c] From ref 1.

deviations from the octahedral symmetry[1] in the inorganic compounds, which would suggest a substantial electric quadrupole splitting. An explanation of this finding maybe that the p electron population in the p_x, p_y, and p_z orbitals of the inorganic tin(IV) series is altogether very small since the orbitals are filled only by covalent effects. This implies a larger s character in tin bonding orbitals and hence shorter Sn–L bonds and larger deviations from the octahedral symmetry for the cis-octahedral inorganic tin sites of Table IX with respect to the trans-octahedral compounds 1–8 of Table VIII. The first implication is consistent with the lower s electron density at the tin nucleus observed for the inorganic compounds of Table IX in comparison with the organotin compounds of Table VIII. The comparison of bond angles shows that the tin site in $SnCl_4\cdot 2detu$,[1] for example, is more distorted than that in $Me_2SnCl_2\cdot 2dmtu$ (Table V). The comparison of the bond lengths for $SnCl_4\cdot 2detu$ (Sn–S = 2.49 and 2.52 Å; Sn–Cl = 2.48, 2.51, 2.55, and 2.58 Å)[1] shows that they are shorter than the corresponding ones in $Me_2SnCl_2\cdot 2dmtu$ (Sn–S = 2.729; Sn–Cl = 2.616 Å).

This possible explanation of Mössbauer and crystallographic data based on a lack of the directional character of the p orbitals for the cis-octahedral tin(IV) compounds of Table IX needs, however, further data to be verified and substantiated.

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Registry No. 1, 90457-51-5; 2, 90457-52-6; 3, 90457-56-0; $Me_2SnCl_2\cdot 2urea$, 90457-50-4; $Me_2SnCl_2\cdot 2dmu$, 36350-67-1; $Me_2SnCl_2\cdot 2detu$, 90388-85-5; $Ph_2SnCl_2\cdot 2deu$, 90388-86-6; $Ph_2SnCl_2\cdot 2detu$, 90388-87-7; $Ph_2SnCl_2\cdot 2tmu$, 90457-53-7; $Me_2SnCl_2\cdot tmu$, 66625-87-4; $Me_2SnCl_2\cdot tmtu$, 90457-54-8; $Ph_2SnCl_2\cdot tmtu$, 90457-55-9; $SnCl_4\cdot 2deu$, 82055-38-7; $SnCl_4\cdot 2tmu$, 21470-10-0; $SnBr_4\cdot 2dmu$, 90457-57-1; $SnBr_4\cdot 2tmu$, 21470-11-1.

Supplementary Material Available: Table VII, giving the least-squares planes, and listings of the structure factor amplitudes with atomic thermal parameters for $Me_2SnCl_2\cdot 2dmtu$, $Ph_2SnCl_2\cdot 2dmtu$, and $Ph_3SnCl\cdot tmu$ (35 pages). Ordering information is given on any current masthead page.

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Ligand Substitution Processes in Tetranuclear Carbonyl Clusters. 7. Molecular Structure and Carbon Monoxide Exchange Processes of $Co_4(CO)_9$(tripod), tripod = 1,1,1-Tris(diphenylphosphino)methane or $HC(PPh_2)_3$

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A kinetic investigation of intermolecular carbon monoxide exchange reactions of $Co_4(CO)_9$(tripod) (tripod = 1,1,1-tris(diphenylphosphino)methane) with ^{13}C-labeled carbon monoxide is reported. The effect of incoming CO ligand concentration was examined by performing reactions under a pressure of carbon monoxide (up to 160 psi of ^{12}CO) employing $Co_4(^{13}CO)_9$(tripod) as substrate molecule. No dependence of the rate of CO incorporation into the tetranuclear cluster with carbon monoxide pressure was noted. Carbon monoxide substitutional parameters (rate constants and activation parameters) for CO displacement in the $Co_4(CO)_9$(tripod) species were found to be quite similar to those previously observed in the parent $Co_4(CO)_{12}$ and its monoligated phosphorus derivatives. These observations taken in toto imply a common mechanistic pathway for CO substitution in all these derivatives, i.e., a CO dissociative process. Reactions carried out utilizing phosphines and phosphites as incoming ligands were found to be complicated by ligand-dependent pathways for CO substitution. Phosphorus ligand substitution occurs stereoselectively at the apical cobalt sites. The crystal and molecular structure of $Co_4(CO)_9$(tripod) has been determined and is discussed in terms of the influence of structural factors on the reactivity of this species as well as in terms of the matching of the tripod ligand framework with the triangular face of the $Co_4(CO)_{12}$ moiety. The title compound forms monoclinic crystals in space group $I2/a$ with $a = 21.943$ (6) Å, $b = 17.289$ (7) Å, $c = 26.137$ (4) Å, $\beta = 105.14$ (2)°, $V = 9585$ (9) Å^3, and $Z = 8$. The discrepancy indices were $R_1 = 0.052$ and $R_2 = 0.051$ for 3001 reflections with $I > 3\sigma(I)$.

Introduction

Rate data for ligand substitution processes of low-valent mononuclear metal carbonyl derivatives are best interpreted in terms of mechanistic pathways identified with dissociative, interchange, or associative mechanisms (eq 1–3).[1,2] Although analogous substitution reactions in-

$$M(CO)_n \rightleftharpoons M(CO)_{n-1} + CO \xrightarrow{L} M(CO)_{n-1}L \text{ (D)} \quad (1)$$

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