clear differences from those in (2), having ∠ClCuP 6° smaller and Cu—P 0·033 Å [8$\sigma$(difference)] shorter. These changes may be attributed to conformational differences. The $CuCl(PPh_3)_3$ molecules in (2) all have ClCuP—C torsional angles (±1°) of 32, 155 and 85°, while they are 57·2, 60·7 and 179·4° in (1). Molecules in $CuCl(PPh_3)_3.3THF$ thus have a general Cu—P rotational conformation which puts one P—C vector more precisely *anti* to the Cu—Cl vector than is found in $CuCl(PPh_3)_3$. These differences are displayed in Fig. 2, prepared using program *BMFIT* (Yuen & Nyburg, 1979).

The Cu—Cl distance in $ClCu(PPh_3)_3.3THF$ does not differ significantly from the average value in (2), but the Cu—P distance is shorter by 8$\sigma$ than the average value [2·351 (4) Å] in (2). Accompanying the shorter Cu—P distance in $ClCu(PPh_3)_3.3THF$ is a larger (115·0°) PCuP′ angle than the corresponding values [109·12 (6)–110·51 (6)°] in (2).

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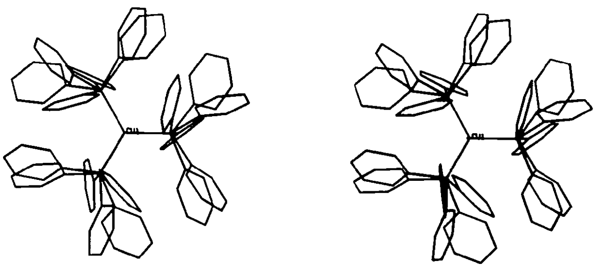

Fig. 2. Stereoview of the best least-squares fit of $CuCl(PPh_3)_3$ found in the unit cell of (1) to the same molecule as found in (2).

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# Di-$\mu_3$-oxo-bis($\mu$-trichloroacetato-*O,O′*)-bis(trichloroacetato)tetrakis[dimethyltin(IV)]

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**Abstract.** $[Sn_4(C_2Cl_3O_2)_4(CH_3)_8O_2]$, $[\{(CH_3)_2Sn(O_2CCCl_3)\}_2O]_2$, $M_r = 2 \times 638{\cdot}3 = 1276{\cdot}6$, triclinic, $P\bar{1}$, $a = 11{\cdot}778$ (5), $b = 10{\cdot}048$ (7), $c = 8{\cdot}773$ (5) Å, $\alpha = 95{\cdot}31$ (2), $\beta = 98{\cdot}07$ (2), $\gamma = 103{\cdot}34$ (2)°, $V = 991{\cdot}7$ (18) Å$^3$, $Z = 1$, $D_x = 2{\cdot}14$ g cm$^{-3}$, $\mu$(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) $= 31{\cdot}0$ cm$^{-1}$, $F(000) = 604$, room temperature, 1652 X-ray diffractometer measurements refined to give $wR = 0{\cdot}069$. The molecules are dimers with $C_{2h}$ symmetry and the structure is virtually identical to those of both $[\{(C_4H_9)_2Sn(O_2CCCl_3)\}_2O]_2$ and $[\{(CH_3)_2Sn(O_2CCF_3)\}_2O]_2$. Both Sn atoms occupy distorted trigonal bipyramidal environments (the methyl groups in the equatorial plane) with one symmetrically bridging trichloroacetate group [Sn—O = 2·236 (11) and 2·235 (13) Å] and one very asymmetric monodentate trichloracetate group. The coordination is completed by one or two further O neighbours. The Cl atoms are disordered.

**Introduction.** $[\{(CH_3)_2Sn(O_2CCCl_3)\}_2O]_2$ was prepared from the attempted recrystallization of $(CH_3)_4Sn_2(O_2CCl_3)_2$ from chloroform. As with $[\{(CH_3)_2Sn(O_3CCF_3)\}_2O]_2$ (Faggiani, Johnson, Brown & Birchall, 1978), heating a chloroform solution of $(CH_3)_4Sn_2(O_2CCl_3)_2$ results in tin–tin cleavage and formation of the title compound as fibrous crystalline needles.

**Experimental.** A cylindrically shaped crystal of radius ~0·1 mm was mounted on a Syntex $P2_1$ diffractometer. Lattice parameters were calculated from the settings of 15 well centred reflections with $7 \leq 2\theta \leq 34°$ and

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Mo $K\alpha$ radiation. Space group was confirmed as $P\bar{1}$ from the successful structure determination. Intensities of 1757 reflections with $2\theta \leq 48°$ were measured using a $\theta$–$2\theta$ scan technique on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation. No correction for absorption was necessary. Standard reflections were measured at regular intervals and showed no significant variation. Of the 1757 unique reflections, 105 were considered 'unobserved', *i.e.* had intensities less than $3\sigma$ where $\sigma$ is the error based on counting statistics.

The positional parameters of the two Sn atoms in the asymmetric unit were determined from a three-dimensional Patterson synthesis. Subsequent difference Fourier syntheses revealed the positional parameters of the remaining non-H atoms. Least-squares refinement on $F$ of the positional parameters and anisotropic temperature factors using *SHELX*76 (Sheldrick, 1976) gave $R_1 = 0{\cdot}086$ and a difference electron density map revealed disorder in the Cl positions. Refinement was continued using two sets of 1/2 site occupancy rotated 60° to each other about the C—C axis. The site occupancy was also refined and this converged at 0·66 to give $R_1 = 0{\cdot}067$ and $wR = 0{\cdot}069$, $w = 1/[\sigma^2(F) + gF^2]$; $g = 0{\cdot}0016$ was used and shown to be satisfactory from weight analysis. An extinction correction given by $F^* = F(1 - 0{\cdot}51 \times 10^{-7}F^2/\sin\theta)$ was applied. The average value of the shift/e.s.d. in the final cycle of refinement was 0·03. Atomic scattering factors were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). The largest peak in the final difference Fourier map (0·85 e Å$^{-3}$) was located in the neighbourhood of the Cl atoms. Methyl H-atom positional parameters were refined but not their temperature factors ($U = 0{\cdot}08$ Å$^2$). The final value of $S = 1{\cdot}56$. Final positional coordinates are given in Table 1.[†]

**Discussion.** Bond lengths and angles are given in Table 2 and the structure is illustrated in Fig. 1. The dimer is essentially identical to those of $[\{(CH_3)_2Sn(O_2CCF_3)\}_2O]_2$ (Faggiani, Johnson, Brown & Birchall (1978) and $[\{(C_4H_9)_2Sn(O_2CCCl_3)\}_2O]_2$ (Graziani, Bombieri, Forsellini, Furlan, Peruzzo & Tagliavini, 1977), the latter having the same space group. Each dimer contains an essentially planar central $Sn_4O_4$ group, two of the four Sn atoms being crystallographically distinct. Both have distorted trigonal bipyramidal coordination with the two methyl groups (mean Sn—C = 2·08 Å) and the bridging O atom (mean Sn—O = 2·05 Å) in the equatorial plane. The

Table 1. *Positional coordinates* (×10$^4$) *with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $U_{eq}$(Å$^2$ × 10$^4$)* |
|---|---|---|---|---|
| Sn(1) | 5264 (1) | 8756 (1) | 969 (1) | 665 |
| Sn(2) | 2191 (1) | 9361 (1) | 487 (1) | 564 |
| O(1) | 2917 (10) | 9660 (9) | 235 (10) | 571 |
| C(1) | 5030 (16) | 7076 (14) | 9233 (18) | 980 |
| C(2) | 5928 (16) | 9719 (18) | 3232 (15) | 959 |
| C(3) | 1191 (15) | 7932 (15) | 8664 (16) | 901 |
| C(4) | 2132 (16) | 547 (16) | 2523 (16) | 906 |
| O(11) | 3938 (10) | 7097 (10) | 1751 (10) | 953 |
| O(12) | 2315 (10) | 7648 (13) | 1907 (10) | 783 |
| C(11) | 3073 (16) | 7036 (13) | 2378 (16) | 842 |
| C(12) | 2677 (15) | 5897 (13) | 3444 (15) | 761 |
| Cl(11) | 2134 (11) | 6526 (9) | 4936 (9) | 895 |
| Cl(12) | 1639 (10) | 4570 (8) | 2395 (11) | 1020 |
| Cl(13) | 3875 (10) | 5241 (10) | 4069 (13) | 1063 |
| Cl(14) | 2597 (20) | 4340 (16) | 2565 (20) | 1198 |
| Cl(15) | 3856 (19) | 6315 (17) | 5007 (18) | 1128 |
| Cl(16) | 1582 (18) | 5904 (19) | 4411 (21) | 1088 |
| O(21) | 2396 (9) | 1141 (9) | −937 (10) | 628 |
| O(22) | 591 (13) | 1231 (13) | −753 (14) | 986 |
| C(21) | 1455 (15) | 1532 (16) | −1332 (16) | 655 |
| C(22) | 1597 (14) | 2669 (13) | −2436 (16) | 794 |
| Cl(21) | 960 (12) | 1851 (10) | −4199 (8) | 1115 |
| Cl(22) | 770 (10) | 3866 (9) | −1984 (11) | 1080 |
| Cl(23) | 3032 (9) | 3678 (9) | −2301 (11) | 1168 |
| Cl(24) | 1657 (20) | 4111 (16) | −1326 (19) | 1208 |
| Cl(25) | 2871 (14) | 2959 (14) | −3309 (16) | 880 |
| Cl(26) | 599 (20) | 2079 (22) | −4033 (21) | 1186 |

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2\cos\beta U_{13} + 2\cos\alpha U_{23} + 2\cos\gamma U_{12})$.

Table 2. *Bond lengths* (Å) *and angles* (°) *for di-$\mu_3$-oxo-bis*(*$\mu$-trichloroacetato*)*-bis*(*trichloroacetato*)*-tetrakis*[*dimethyltin*(IV)] *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| Sn coordination | | | |
| Sn(1)—O(1) | 2·069 (11) | Sn(2)—O(1) | 2·032 (1) |
| Sn(1)—O(1$^{i}$) | 2·115 (11) | Sn(2)—O(12) | 2·236 (11) |
| Sn(1)—O(11) | 2·235 (13) | Sn(2)—O(21) | 2·262 (9) |
| Sn(1)—C(1) | 2·106 (14) | Sn(2)—C(3) | 2·067 (13) |
| Sn(1)—C(2) | 2·085 (14) | Sn(2)—C(4) | 2·072 (14) |
| Sn(1)—Sn(1$^{i}$) | 3·277 (2) | Sn(2)—Sn(1) | 3·779 (2) |
| Sn(1)—O(1)—Sn(2) | 134·9 (4) | O(12)—Sn(2)—O(21) | 170·3 (1) |
| O(1)—Sn(1)—C(1) | 103·5 (5) | O(1)—Sn(2)—C(3) | 107·7 (6) |
| O(1)—Sn(1)—C(2) | 104·1 (6) | O(1)—Sn(2)—C(4) | 107·6 (6) |
| O(11)—Sn(1)—O(1$^{i}$) | 88·8 (2) | C(3)—Sn(2)—C(4) | 144·6 (7) |
| C(1)—Sn(1)—C(2) | 150·3 (7) | O(21)—Sn(2)—O(1) | 78·9 (2) |
| O(11)—Sn(1)—C(1) | 77·1 (5) | O(12)—Sn(2)—O(1) | 91·5 (2) |
| O(11)—Sn(1)—C(2) | 92·7 (4) | O(21)—Sn(2)—C(3) | 94·2 (4) |
| | | O(21)—Sn(2)—C(4) | 94·7 (4) |
| $\mu$-Trichloroacetato | | | |
| C(11)—O(11) | 1·216 (22) | C(12)—Cl(11) | 1·677 (17) |
| C(11)—O(12) | 1·242 (20) | C(12)—Cl(12) | 1·680 (15) |
| C(11)—C(12) | 1·574 (18) | C(12)—Cl(13) | 1·733 (19) |
| C(11)—O(11)—Sn(1) | 136·3 (9) | C(11)—C(12)—Cl(11) | 111·2 (9) |
| C(11)—O(12)—Sn(2) | 137·6 (9) | C(11)—C(12)—Cl(12) | 109·6 (8) |
| O(11)—C(11)—O(12) | 119·9 (8) | C(11)—C(12)—Cl(13) | 108·8 (10) |
| C(12)—C(11)—O(11) | 122·1 (6) | | |
| C(12)—C(11)—O(12) | 115·8 (6) | | |
| Trichloroacetate 2 | | | |
| C(21)—O(21) | 1·273 (18) | C(22)—Cl(21) | 1·670 (15) |
| C(21)—O(22) | 1·191 (19) | C(22)—Cl(22) | 1·764 (19) |
| C(21)—C(22) | 1·561 (12) | C(22)—Cl(23) | 1·740 (18) |
| C(21)—O(21)—Sn(2) | 115·1 (8) | C(21)—C(22)—Cl(21) | 105·3 (8) |
| O(21)—C(21)—O(22) | 124·1 (9) | C(21)—C(22)—Cl(22) | 110·4 (9) |
| C(22)—C(21)—O(21) | 113·9 (9) | C(21)—C(22)—Cl(23) | 115·0 (9) |
| C(22)—C(21)—O(22) | 121·1 (9) | | |

(i) Denotes symmetry-related atom.

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[†] Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43891 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

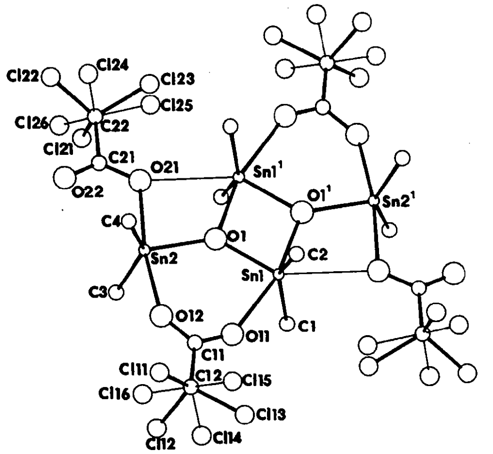

Fig. 1. The molecular structure of di-$\mu_3$-oxo-bis($\mu$-trichloroacetato-*O,O'*)-bis(trichloroacetato)tetrakis[dimethyltin(IV)]. The H atoms have been omitted for clarity. The asymmetric unit bears the numbering scheme.

axial Sn—O bonds are slightly longer (mean Sn—O = 2·21 Å). Although the Sn-atom environments are similar, the trichloroacetate ions are quite different. One forms a symmetrical bridge between Sn(1) and Sn(2), mean Sn—O = 2·235 Å. The other is bonded only to Sn(2) [Sn(2)—O(21) = 2·262 Å] making the ion very asymmetric. O(21) also forms a very weak bond to Sn($1^i$), Sn($1^i$)···O(21) = 2·70 Å. The other O atom of this ion, O(22), forms a weak bond to Sn($2^i$) in the adjacent dimer [Sn($2^i$)···O(22) = 3·09 Å] linking the independent molecules into a ladder-type structure running along the *a* axis.

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# Structure of Bis(2,2',2''-triaminotriethylamine-*N,N',N''*)-$\mu$-(triethylenetetramine-*N,N',N'',N'''*)-dinickel(II) Tetraperchlorate

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**Abstract.** $\mu$-[2,2'-(Ethylenediamino)di(ethylamine)-*N,N',N'',N'''*]-bis(2,2',2''-nitrilotriethylamine)dinickel(II) tetraperchlorate, $[Ni_2(C_6H_{18}N_4)(C_6H_{18}N_4)_2](ClO_4)_4$, $M_r$=954·0, monoclinic, $C2/c$, $a$=20·285(4), $b$ = 18·112 (4), $c$ = 15·045 (3) Å, $\beta$ = 135·70 (1)°, $V$ = 3861 (3) Å$^3$, $Z$ = 4, $D_x$ = 1·63 g cm$^{-1}$, Mo $K\alpha$ radiation, $\lambda$ = 0·71069 Å, $\mu$ = 13·33 cm$^{-1}$, $F(000)$ = 1992, $T$ = 293 K, $R$ = 0·042, $wR$ = 0·043, 1564 unique reflections. The structure consists of pairs of octahedrally coordinated $Ni^{II}$ ions and isolated perchlorate ions. Each tren ligand (tren ≡ 2,2',2''-triaminotriethylamine) occupies four coordination sites on each $Ni^{II}$ ion, spanning a pair of adjacent octahedral faces. The trien ligand (trien ≡ triethylenetetramine) bridges between two Ni ions, with two N atoms coordinating in a *cis* fashion to each Ni atom, completing the Ni coordination spheres.

**Introduction.** The system $Ni^{II}$–tren has been the subject of several kinetic studies in solution, including the rate of water exchange in the aqua complex (Rablen, Dodgen & Hunt, 1972) and substitution of water by ammonia (Jones, Billo & Margerum, 1970). In the water exchange study, two different exchange rates were observed, leading the authors to propose a *cis*-octahedral arrangement for the $Ni(tren)(H_2O)_2^{2+}$ species. Other authors have suggested tetrahedral (Bertsch, Fernelius & Block, 1958) or trigonal bipyramidal (Jonassen & Thilemann, 1963). In this paper, we present solid-state structural results for the compound bis(triaminoethylamine)(triethylenetetramine)dinickel(II) perchlorate, $C_{18}H_{54}N_{12}Ni_2^{4+}.4ClO_4^-$ (I), supporting the concept of a *cis*-octahedral arrangement. During an earlier period, we attempted to solve the structure, but were unsuccessful. In order to

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