proche d'un carré. En effet, les liaisons Pt(1)—N(12) et Pt(1)—N(14) sont perpendiculaires entre elles et ont pratiquement la même longueur, tandis que leurs homologues issues de Pt(2) sont identiques et font entre elles un angle de 90,6 (2)°. Les angles Cl—Pt—N (Tableau 2) indiquent que, dans le polyèdre de coordination de chaque atome métallique, la droite Cl—Pt—Cl est presque perpendiculaire au plan des atomes d'azote. Les distances Pt—N ont pour longueurs extrêmes 2,049 (4) et 2,059 (4) Å et les distances Pt—Cl 2,302 (2) et 2,309 (2) Å. On trouve des longueurs comparables pour leurs homologues respectives dans les trois formes isomères du diamminedichlorodi-hydroxyplatine(IV) (Kuroda, Neidle, Ismail & Sadler, 1983), dans le chlorure de *trans*-dichlorobis(propane-diamine-1,3)platine(IV) tétrahydrate (Delafontaine, Toffoli, Khodadad & Rodier, 1988) ou dans le bipyridyl-2,2' tétrachloroplatine(IV) (Hambley, 1986). Ainsi, dans les trois variétés du premier composé cité, les longueurs extrêmes des liaisons Pt—N sont de 2,028 (6) et de 2,056 (5) Å et celles des liaisons Pt—Cl de 2,303 (1) et de 2,325 (3) Å.

Les deux anions méthanesulfonate ont des géométries très voisines. Tous les deux admettent le plan $y = \frac{1}{2}$ pour plan de symétrie. De plus, les différences les plus importantes entre les longueurs et les angles des liaisons homologues restent comparables aux incertitudes. Les distances S—O appartiennent à l'intervalle 1,439 (7)–1,464 (6) Å. Les mêmes distances mesurent 1,440 (2) et 1,443 (2) Å dans le méthane-sulfonate d'ammonium (Wei, 1986) et sont comprises entre 1,429 (5) et 1,456 (4) Å dans le méthanesulfonate

de calcium (Charbonnier, Faure & Loiseleur, 1977). Pour les distances S—C, on trouve 1,770 (7) et 1,774 (8) Å dans le composé étudié, 1,750 (3) Å dans $NH_4(CH_3SO_3)$, 1,760 (8) et 1,748 (6) Å dans $Ca(CH_3SO_3)_2$.

Outre les interactions entre les ions, la cohésion de la structure fait intervenir de nombreuses liaisons hydrogène. Ces liaisons ont été représentées sur la Fig. 1. Leurs longueurs sont rapportées dans le Tableau 2.

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Structure of (p-Chlorophenyl)bis(quinolin-8-olato)(p-tolyl)tin(IV)

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Abstract. $|Sn(C_6H_4Cl)(C_7H_7)(C_9H_6NO)_2|$, $M_r = 609 \cdot 7$, monoclinic, $C2/c$, $a = 11 \cdot 708$ (1), $b = 17 \cdot 869$ (3), $c = 13 \cdot 007$ (2) Å, $\beta = 93 \cdot 65$ (2)°, $V = 2716$ (1) Å³, $Z = 4$, $D_m = 1 \cdot 45$, $D_x = 1 \cdot 49$ g cm⁻³, graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0 \cdot 7107$ Å), $\mu = 9 \cdot 72$ cm⁻¹, $F(000) = 1224$, $T = 297$ K,

$R = 0.026$ for 2590 unique reflections. The coordination geometry around Sn is octahedral with the p-chlorophenyl and p-tolyl groups oriented cis to each other and the two quinolinolato ligands unequivocally engaged in chelation, a bonding mode which appears to be characteristic of the ligand in metal coordination.

Introduction. Six-coordinate diorganotin(IV) compounds containing neutral (Ch) or uninegative (Ch') bidentate chelate ligands, as in the formulations R_2SnX_2(Ch) (X = halide or pseudohalide) and R_2Sn-(Ch')$_2$, respectively, are known to adopt cis, trans or distorted octahedral structures, depending on the influence of substituents in the carbon- and hetero-atom-donor ligands (Kumar Das, Yap & Smith, 1987). For the distorted structures in which the C–Sn–C bond angles fall in the range 135–155°, the geometry has been labelled skewed-trapezoidal bipyramid (STB) and viewed as a discrete polytopal form by Kepert (1977). A re-interpretation of several distorted trans-|SnR$_2$| octahedral geometries as STB has recently been reported (Ng, Chen, Kumar Das & Mak, 1987). Thus n-PrEtSn(2-Meoxin)$_2$ (oxin = 8-quinolinolato) has been shown to have an STB geometry (Kumar Das, Chen, Yap & Sinn, 1984), in sharp contrast to the cis-[SnR$_2$] octahedral geometries which characterize Me$_2$Sn-(oxin)$_2$ (Schlemper, 1967) and [(Me$_3$Si)$_2$CH]MeSn-(oxin)$_2$ (Ng, 1981). A further example of substituent influence is seen in the change from trans- to cis-|SnR$_2$| octahedral geometry in going from Ph$_2$SnCl$_2$(bpy) (Harrison, King & Richards, 1974) to (p-tolyl)$_2$SnCl$_2$-(bpy) (Kumar Das, Chen, Yap & Mak, 1986). To date, there has been no crystal-structure report of a diaryltin bis(quinolin-8-olate), although based on ^{119}Sn Mössbauer evidence such compounds have been assigned cis-|SnR$_2$| octahedral geometries (Bancroft & Platt, 1972). The title compound constitutes the first X-ray structure of a diorganotin bis(quinolin-8-olate) containing mixed aryl groups on tin.

Experimental. 6 mmol (p-ClC$_6$H$_4$)(p-MeC$_6$H$_4$)SnO and 12·mmol quinolin-8-ol were heated together in 200 ml CHCl$_3$ under reflux until the solution cleared. Following filtration and concentration, about 20 ml MeOH were added. Slow evaporation of the resultant solution yielded crystals suitable for X-ray analysis. (Found: C, 60·0; H, 3·71; N, 4·35; calculated for C$_{31}$H$_{23}$Cl-N$_2$O$_2$Sn: C, 59·95; H, 3·77; N, 4·5%.) Density measured by flotation method in KI/H$_2$O mixture; crystal used was a yellow flattened octahedron (0·27 × 0·25 × 0·15 mm) mounted on a Picker FACS-I diffractometer; 15 reflections with $30 < 2\theta < 35°$ used to obtain lattice parameters; Lorentz, polarization and empirical absorption corrections applied, max./min. values 99·88/93·69; 2590 unique reflections measured with |(sinθ)/λ|$_{max}$ = 0·6231 Å^{-1}; h, k, l = −13 to 14, 0 to 23, 0 to 16, respectively; 331 reflections were

unobserved with $F_o^2 < 3\sigma(F_o^2)$; three standard reflections showed no significant crystal decay throughout data collection; structure was solved by Patterson syntheses from which the y coordinate of the Sn atom was obtained in space group $C2/c$, the remaining atoms, including the H atoms, were located by difference Fourier syntheses. Full-matrix least-squares refinement

Table 1. *Positional and equivalent isotropic thermal parameters and their e.s.d.'s*

The starred atom was refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter, B_{eq}, defined as:

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Sn	0·000	0·13903 (1)	0·250	3·383 (4)
Cl	0·4038 (3)	−0·0809 (2)	0·0896 (3)	12·74 (9)
O	−0·0868 (2)	0·1630 (1)	0·1090 (1)	4·43 (4)
N	0·0981 (2)	0·2387 (1)	0·1824 (2)	4·05 (5)
C(2)	0·1883 (3)	0·2751 (2)	0·2212 (3)	5·37 (7)
C(3)	0·2442 (3)	0·3286 (2)	0·1645 (3)	6·93 (9)
C(4)	0·2057 (3)	0·3432 (2)	0·0656 (3)	6·69 (9)
C(5)	0·0593 (4)	0·3176 (2)	−0·0789 (3)	6·75 (8)
C(6)	−0·0338 (4)	0·2787 (2)	−0·1116 (3)	7·3 (1)
C(7)	−0·0839 (3)	0·2252 (2)	−0·0499 (2)	5·68 (8)
C(8)	−0·0413 (2)	0·2117 (2)	0·0472 (2)	4·19 (6)
C(9)	0·0582 (2)	0·2529 (2)	0·0842 (2)	3·97 (5)
C(10)	0·1087 (3)	0·3055 (2)	0·0212 (2)	5·12 (6)
C(11)	0·1332 (2)	0·0676 (2)	0·2017 (2)	3·88 (5)
C(12)	0·2375 (3)	0·0605 (2)	0·2566 (3)	4·85 (7)
C(13)	0·3212 (3)	0·0136 (2)	0·2225 (3)	6·05 (8)
C(14)	0·3024 (3)	−0·0263 (2)	0·1326 (3)	6·16 (8)
C(15)	0·1994 (4)	−0·0208 (2)	0·0783 (3)	6·54 (9)
C(16)	0·1158 (3)	0·0254 (2)	0·1132 (3)	5·77 (8)
C(17)*	0·394	−0·076	0·095	

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Sn–O	2·084 (2)	C(5)–C(10)	1·407 (5)
Sn–N	2·322 (2)	C(6)–C(7)	1·401 (5)
Sn–C(11)	2·140 (3)	C(7)–C(8)	1·349 (4)
Cl–C(14)	1·660 (4)	C(8)–C(9)	1·434 (4)
O–C(8)	1·320 (3)	C(9)–C(10)	1·403 (4)
N–C(2)	1·314 (4)	C(11)–C(12)	1·381 (4)
N–C(9)	1·356 (3)	C(11)–C(16)	1·380 (4)
C(2)–C(3)	1·395 (5)	C(12)–C(13)	1·384 (4)
C(3)–C(4)	1·360 (6)	C(13)–C(14)	1·376 (5)
C(4)–C(10)	1·412 (5)	C(14)–C(15)	1·362 (5)
C(5)–C(6)	1·340 (6)	C(15)–C(16)	1·379 (5)

O–Sn–N	74·59 (7)	O–C(8)–C(7)	123·2 (3)
O–Sn–C(11)	100·82 (9)	O–C(8)–C(9)	119·0 (2)
N–Sn–C(11)	87·65 (9)	C(7)–C(8)–C(9)	117·8 (3)
Sn–O–C(8)	118·6 (2)	N–C(9)–C(8)	116·3 (2)
Sn–N–C(2)	129·7 (2)	N–C(9)–C(10)	122·9 (3)
Sn–N–C(9)	110·5 (2)	C(8)–C(9)–C(10)	120·8 (3)
C(2)–N–C(9)	119·3 (3)	C(4)–C(10)–C(5)	125·3 (3)
Sn–C(11)–C(12)	122·7 (2)	C(4)–C(10)–C(9)	116·0 (3)
Sn–C(11)–C(16)	119·9 (2)	C(5)–C(10)–C(9)	118·7 (3)
C(12)–C(11)–C(16)	117·4 (3)	C(11)–C(12)–C(13)	120·7 (3)
N–C(2)–C(3)	121·9 (3)	C(12)–C(13)–C(14)	120·5 (3)
C(2)–C(3)–C(4)	119·5 (3)	Cl–C(14)–C(13)	120·8 (4)
C(3)–C(4)–C(10)	120·4 (3)	Cl–C(14)–C(15)	119·8 (3)
C(6)–C(5)–C(10)	119·5 (3)	C(13)–C(14)–C(15)	119·4 (3)
C(5)–C(6)–C(7)	122·3 (3)	C(14)–C(15)–C(16)	119·8 (3)
C(6)–C(7)–C(8)	121·0 (3)	C(11)–C(16)–C(15)	122·1 (3)

of 173 parameters based on F gives $R = 0.026$, $wR = 0.033$, $w = 4(F_o)^2/|\sigma(F_o)^2|^2$, where $|\sigma(F_o)^2|^2 = |S^2(C+R^2B) + P(F_o)^2|/Lp^2$ and $P =$ experimental instability factor, $S =$ scan rate, $C =$ total integrated peak count, $R =$ ratio of scan time to background counting time, $B =$ total background count, $Lp =$ Lorentz–polarization factor, and goodness of fit of 1·160. With only one crystallographically independent phenyl group in space group $C2/c$, disorder of the chloro and methyl substituents is required. The methyl substituent was fixed symmetrically 1·50 Å from the phenyl carbon to which it is bonded with occupancy set to 1–α, where α is the occupancy of the chloro substituent, and with a temperature factor identical to that of the chloro substituent. The positional, thermal and occupancy parameters of the chloro group were refined, leading to a reasonable temperature factor, C–Cl bond length and occupancy of 0·413 (3). This is satisfactorily close to the 1(chlorophenyl):1(tolyl) ratio found by chemical analysis for the bulk sample. Refinement in space group Cc converged at higher R values than for $C2/c$. From difference Fourier maps it was apparent that the Cl and CH_3 remained disordered; thus space group Cc was discarded. Final difference map showed maximum density of 0·46 e Å^{-3} near the Sn atom and a minimum density of -0.28 e Å^{-3}; maximum least-squares shift/e.s.d. = 0·02 in the last cycle; atomic scattering factors were obtained from Cromer & Waber (1974), anomalous dispersion for non-H atoms included in F_c using Cromer (1974); computer programs used: *TEXRAY* package (Molecular Structure Corporation, 1985) on a PDP 11/73 minicomputer and *SDP* (Enraf–Nonius, 1979) on a PDP 11/44 computer. Atomic coordinates and thermal
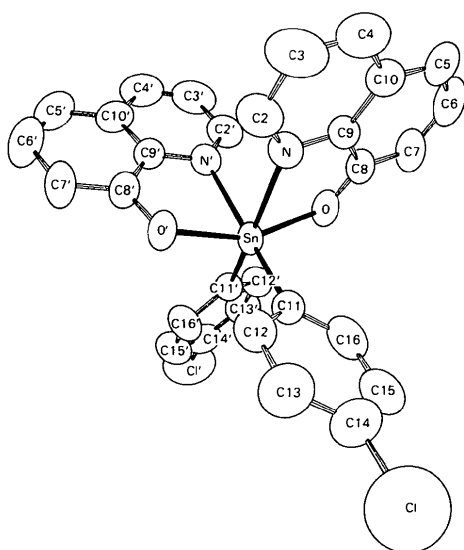
Table 3. *Comparison of selected bond dimensions of the title compound* (1) *with those of* $Me_2Sn(oxin)_2$ (2) *and n-PrEtSn(2-Meoxin)$_2$* (3)

Compound	(1)	(2)	(3)
Coordination geometry	*cis*-Octahedral	*cis*-Octahedral	STB
Sn C (Å)	2·140 (3)	2·15 (2), 2·17 (2)	2·145 (8), 2·089 (8)
Sn- O (Å)	2·084 (2)	2·10 (1), 2·11 (1)	2·066 (4), 2·066 (4)
Sn N (Å)	2·322 (2)	2·31 (1), 2·38 (1)	2·542 (5), 2·597 (6)
O - Sn- N (°)	74·59 (7)	73·4,* 73·7*	70·9 (2), 149·7 (2)
Angles at Sn (°)	74·5 (7)–106·8 (7)	73·4*–110·7*	70·9 (2)–139·3 (2)
Interplanar angle (°) of chelate rings	88·9 (5)	78·2*	8·7*

* E.s.d.'s not available.

parameters are listed in Table 1, and bond distances and angles in Table 2.*

Discussion. As shown in Fig. 1, the title compound forms a discrete hexacoordinate complex with the oxin ligand in a chelating mode. The geometry at the metal centre is octahedral with the *p*-chlorophenyl and *p*-tolyl groups in *cis* array, as predicted from the ^{119}Sn Mössbauer data of the compound [quadrupole splitting (80 K), 1·79 mm s^{-1}; calculated $(-)1·80$ mm s^{-1}]. The Sn atom lies on a twofold rotation axis in as much as the Cl and Me ring substituents are indistinguishable on account of disorder. A comparison of some selected bond lengths and angles around Sn in the title compound with those in n-PrEtSn(2-Meoxin)$_2$ and $Me_2Sn(oxin)_2$ (Table 3) shows no large deviations from the $Me_2Sn(oxin)_2$ case. The C–Sn–C bond angles in the title compound, however, are closer to the idealized *cis* angle of 90°. Thus the *para* substituents in the aryl rings, unlike the 2-methyl substituent in the oxin ligand, exert no steric influence which destabilizes the preferred *cis*-[SnR$_2$] octahedral structure (Kepert, 1976, 1977; Tse, Sham & Bancroft, 1979) in favour of the STB.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51660 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. A perspective view of [Sn(p-ClC$_6$H$_4$)(p-MeC$_6$H$_4$)-(C$_9$H$_6$NO)$_2$].

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Structures of the *cis* and *trans* Isomers of the Bis(1-thia-4,7-diazacyclononane)cobalt(III) Cation

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Abstract. *trans*-Bis(1-thia-4,7-diazacyclononane)-cobalt(III) trifluoromethanesulfonate, (I), *trans*-[Co-$(C_6H_{14}N_2S)_2](CF_3SO_3)_3$, $M_r = 798.6$, triclinic, $P\bar{1}$, $a = 10.422$ (2), $b = 10.561$ (2), $c = 14.352$ (4) Å, $\alpha = 105.83$ (2), $\beta = 102.57$ (2), $\gamma = 103.29$ (2)°, $V = 1411.1$ Å^3, $Z = 2$, $D_x = 1.878$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 10.27$ cm^{-1}, $F(000) = 812$, $T = 294$ K. Final $R = 0.038$ for 4044 reflections. *cis*-Bis(1-thia-4,7-diazacyclononane)cobalt(III) tetraaqualithium(I) bromide monohydrate, (II), *cis*-[Co$(C_6H_{14}N_2S)_2$]-[Li$(H_2O)_4$]Br$_4$.1H$_2$O, $M_r = 768.1$, monoclinic, *C2*, $a = 13.426$ (5), $b = 9.455$ (2), $c = 11.504$ (4) Å, $\beta = 113.15$ (2)°, $V = 1342.8$ Å^3, $Z = 2$, $D_x = 1.899$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 66.32$ cm^{-1}, $F(000) = 760$, $T = 294$ K. Final $R = 0.026$ for 1183 reflections. The two tridentate ligands coordinate with a *trans* arrangement of the S atoms and ring conformations ($\lambda\delta\lambda$, $\lambda\delta\lambda$) in (I) and a *cis* arrangement and ring conformations ($\lambda\lambda\lambda$, $\lambda\lambda\lambda$) in (II). The *trans* Co—S bonds in (I), 2.251 (1) and 2.246 (1) Å, are longer than the *cis* Co—S bonds in (II), 2.217 (2) Å. Molecular-mechanics calculations show that the *cis* isomer is slightly more stable than the *trans* and also suggest that the difference in Co—S bond lengths is a consequence of an electronic, rather than a steric, *trans* effect.

Introduction. Metal complexes of the macrocyclic ligand 1-thia-4,7-diazacyclononane (tasn), a nine-membered ring with one thioether-S and two amine-N donor atoms, have been the subject of much attention recently (Gahan, Hambley, Searle, Bjerrum & Larsen, 1988, and references therein). Two geometric isomers are possible for octahedral |M(tasn)$_2$|$^{x+}$ complexes, designated *cis* and *trans* according to the arrangement of the S atoms about the metal. Structures of both |Cu(tasn)$_2$|(NO$_3$)$_2$ and |Ni(tasn)$_2$|(NO$_3$)$_2$ have revealed the *trans* isomer (Boeyens, Dobson & Hancock, 1985; Hart, Boeyens, Michael & Hancock, 1983). Preparation of the Co^{III} complex was first described by Gahan, Lawrance & Sargeson (1982) and they and Nonoyama & Ishida (1984) obtained spectroscopic evidence for the existence of more than one isomer. However, separation of the isomers could not be effected chromatographically. We recently reported the structure of the perchlorate salt of the Co^{III} complex obtained in the earlier preparation and showed that it too had the *trans* geometry (Hambley & Gahan, 1986). Extensive surveys of the crystals using visual, crystallographic and density separation techniques did not locate another crystal type. In order to investigate further the possible existence of the *cis* isomer an