$[Cu(C_{19}H_{20}N_4S_2)]ClO_4$

Related literature. The structure determination is part of our studies of transition-metal complexes derived from potentially quadridentate NSSN ligands (Castiñerias, Hiller, Strähle, Paredes & Sordo, 1985; Castiñeiras, Carballo, Bermejo, Gayoso, Molleda, Hiller & Strähle, 1988; Castiñeiras, Carballo, Hiller, Montero, Pena & Strähle, 1990; Castiñeiras, Hiller, Strähle, Carballo, Bermejo & Gayoso, 1990; Castiñeiras, Carballo, Hiller & Strähle, 1990a,b, 1991; Hiller, Strähle, Castiñeiras, Carballo, Bermejo & Gayoso, 1990).

The structural parameters of [Cu(BBDHP)]ClO$_4$ can also be compared with those found in [Cu(BBDHP)](PF$_6$)$_{0.66}$(BF$_4$)$_{0.34}$ (Schilstra, Birker, Verschoor & Reedijk, 1982).

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Structure of Dichloro(iodo)bis(triphenylphosphine oxide)thallium(III) at 223 K

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Abstract. [Tl(Cl)$_2$(I){P(C$_6$H$_5$)O}$_2$], $M_r = 958.77$, monoclinic, $P2_1/c$, $a = 14.738$ (1), $b = 14.466$ (6), $c = 17.194$ (1) Å, $\beta = 107.98$ (1)°, $V = 3486.7$ Å^3, $Z = 4$, $D_x = 1.826$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.70930$ Å, $\mu = 58.3$ cm^{-1}, $F(000) = 1840$, $T = 223$ K, final $R = 0.062$ for 4967 significant $[I > 3\sigma(I)]$ reflections. The structure consists of discrete TlCl$_2$I(tppo)$_2$ molecules (tppo = triphenylphosphine oxide) which have a distorted trigonal bipyramidal geometry. The Tl atom is coordinated to two Cl atoms and an I atom in equatorial positions, Tl—Cl = 2.412 (2) and 2.400 (5) Å, and Tl—I = 2.635 (2) Å, and by two tppo ligands in axial positions, Tl—O = 2.38 (2) Å. The crystal structure is isotypic with those of TlBr$_3$(tppo)$_2$, TlBr$_2$I(tppo)$_2$, TlBrI$_2$(tppo)$_2$ and TlClBrI(tppo)$_2$.

Experimental. A yellow single crystal of approximate dimensions 0.30 × 0.20 × 0.15 mm was sealed in a glass fibre. Because the crystals decompose at room temperature all X-ray investigations were performed at 223 K. The structure was solved using direct methods which revealed the positions of all non-H atoms. In the final full-matrix least-squares refinement all non-H atoms were assigned aniso-tropic temperature parameters, and the calculated

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Table 1. Data-collection and structure-refinement parameters

Crystal shape	Prism
Diffractometer used	CAD-4, Enraf–Nonius
Method of intensity measurement	ω/θ
No. and θ range ( ) of reflections for lattice parameters	25, 12–18
Method used for absorption correction	DIFABS (Walker & Stuart, 1983)
Minimum absorption correction	0·800
Maximum absorption correction	1·240
Average absorption correction	0·991
Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurement (Å^{-1})	0·62
Range of h, k and l	$0 \to 18$, $0 \to 17$, $-21 \to 21$
Standard reflections	$\overline{4}6\overline{7}$, $\overline{1}04$, $7\overline{2}8$
Interval (h)	1, no intensity variation
Total No. of reflections measured; θ range ( )	7328; 3–26 (140 unobserved reflections, 300 systematic absences included)
No. of unique reflections, R_{int}	6784, 0·018
No. of observed reflections	4967 with $I > 3\sigma(I)$
Method used to solve structure	Direct methods
Use of F or F^2 in LS refinement	F
Method of locating H atoms	Calculated in idealized positions with C—H = 0·95 Å
Weighting scheme	$1/\sigma^2$
Parameters refined	397
R	0·062
wR	0·075
Ratio of max. LS shift to e.s.d. (Δ/ρ)	0·001
Max. height in final ΔF map (e Å^{-3})	1·519 (close to Tl)
Error in an observation of unit weight	6·88
Sources of atomic scattering factors	International Tables for X-ray Crystallography (1974, Vol. IV, Table 2.2A)
Computer used	MicroVAX II
Programs used	SHELXS86 (Sheldrick, 1986) VAX/SDP, version 3.0 (Frenz, 1978)

Fig. 1. View of the molecule illustrating the atom labelling.
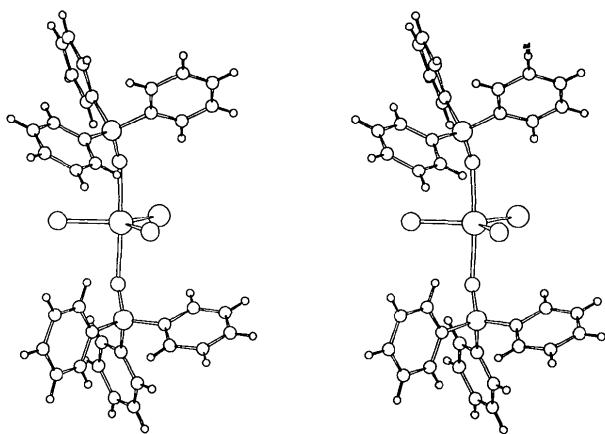
Fig. 2. Stereoscopic view.

Table 2. Positional and equivalent isotropic thermal parameters U_{eq} (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Tl	0·28135 (4)	0·03401 (4)	0·87845 (3)	0·0295 (2)
I	0·4582 (1)	0·0193 (1)	0·8751 (1)	0·111 (1)
Cl(1)	0·1463 (4)	0·0481 (4)	0·7565 (3)	0·075 (3)
Cl(2)	0·2592 (3)	0·0386 (3)	1·0109 (2)	0·059 (2)
P(1)	0·2849 (2)	0·2878 (2)	0·9221 (2)	0·027 (2)
P(2)	0·2003 (2)	−0·2127 (3)	0·8788 (2)	0·030 (2)
O(1)	0·2935 (7)	0·1982 (7)	0·8814 (6)	0·044 (5)
O(2)	0·2565 (7)	−0·1289 (7)	0·8732 (7)	0·056 (6)
C(11)	0·3444 (9)	0·285 (1)	1·0310 (8)	0·031 (6)
C(12)	0·429 (1)	0·236 (1)	1·0584 (9)	0·040 (8)
C(13)	0·477 (1)	0·237 (1)	1·141 (1)	0·057 (9)
C(14)	0·445 (1)	0·283 (1)	1·195 (1)	0·057 (9)
C(15)	0·361 (1)	0·330 (1)	1·168 (1)	0·063 (9)
C(16)	0·310 (1)	0·331 (1)	1·0851 (9)	0·045 (8)
C(21)	0·3376 (8)	0·3797 (9)	0·8809 (8)	0·027 (6)
C(22)	0·3743 (9)	0·459 (1)	0·9229 (9)	0·039 (7)
C(23)	0·411 (1)	0·528 (1)	0·886 (1)	0·045 (8)
C(24)	0·414 (1)	0·517 (1)	0·806 (1)	0·042 (7)
C(25)	0·379 (1)	0·439 (1)	0·7650 (8)	0·040 (7)
C(26)	0·3397 (9)	0·369 (1)	0·8002 (8)	0·031 (7)
C(31)	0·1632 (9)	0·320 (1)	0·9081 (8)	0·031 (6)
C(32)	0·135 (1)	0·413 (1)	0·900 (1)	0·062 (9)
C(33)	0·041 (1)	0·435 (1)	0·891 (1)	0·08 (1)
C(34)	−0·025 (1)	0·365 (1)	0·886 (1)	0·058 (9)
C(35)	0·003 (1)	0·276 (1)	0·894 (1)	0·054 (9)
C(36)	0·096 (1)	0·253 (1)	0·905 (1)	0·048 (8)
C(41)	0·1960 (9)	−0·2912 (9)	0·7965 (8)	0·029 (6)
C(42)	0·2418 (9)	−0·267 (1)	0·7409 (8)	0·034 (7)
C(43)	0·240 (1)	−0·329 (1)	0·6779 (8)	0·050 (8)
C(44)	0·193 (1)	−0·413 (1)	0·6706 (9)	0·048 (8)
C(45)	0·148 (1)	−0·437 (1)	0·7269 (9)	0·048 (8)
C(46)	0·149 (1)	−0·376 (1)	0·7888 (8)	0·044 (7)
C(51)	0·2600 (9)	−0·274 (1)	0·9723 (8)	0·036 (7)
C(52)	0·215 (1)	−0·343 (1)	1·0033 (9)	0·045 (8)
C(53)	0·266 (1)	−0·394 (1)	1·072 (1)	0·071 (9)
C(54)	0·362 (1)	−0·373 (2)	1·107 (1)	0·09 (1)
C(55)	0·406 (1)	−0·305 (2)	1·079 (1)	0·09 (1)
C(56)	0·355 (1)	−0·257 (2)	1·0116 (9)	0·060 (8)
C(61)	0·0807 (8)	−0·1925 (9)	0·8792 (7)	0·024 (5)
C(62)	0·066 (1)	−0·139 (1)	0·9408 (8)	0·041 (7)
C(63)	−0·024 (1)	−0·122 (1)	0·9452 (9)	0·048 (8)
C(64)	−0·102 (1)	−0·160 (1)	0·8874 (9)	0·046 (8)
C(65)	−0·090 (1)	−0·212 (1)	0·827 (1)	0·051 (8)
C(66)	0·001 (1)	−0·228 (1)	0·8221 (9)	0·048 (8)

Table 3. Selected distances (Å) and angles (°)

Tl—I	2·635 (2)		P(1)—C(21)	1·79 (1)
Tl—Cl(1)	2·412 (5)		P(1)—C(31)	1·80 (1)
Tl—Cl(2)	2·400 (5)		P(2)—O(2)	1·49 (1)
Tl—O(1)	2·38 (2)		P(2)—C(41)	1·81 (1)
Tl—O(2)	2·38 (2)		P(2)—C(51)	1·81 (1)
P(1)—O(1)	1·50 (1)		P(2)—C(61)	1·79 (1)
P(1)—C(11)	1·81 (1)			

I—Tl—Cl(1)	123·0 (2)		O(1)—P(1)—C(21)	110·3 (7)
I—Tl—Cl(2)	116·7 (2)		O(1)—P(1)—C(31)	112·7 (6)
I—Tl—O(1)	90·6 (3)		C(11)—P(1)—C(21)	107·2 (6)
I—Tl—O(2)	93·6 (3)		C(11)—P(1)—C(31)	106·8 (6)
Cl(1)—Tl—Cl(2)	120·3 (2)		C(21)—P(1)—C(31)	107·0 (6)
Cl(1)—Tl—O(1)	88·3 (2)		O(2)—P(2)—C(41)	110·4 (8)
Cl(1)—Tl—O(2)	88·5 (3)		O(2)—P(2)—C(51)	109·3 (6)
Cl(2)—Tl—O(1)	89·1 (3)		O(2)—P(2)—C(61)	115·8 (6)
Cl(2)—Tl—O(2)	90·0 (3)		C(41)—P(2)—C(51)	106·1 (6)
O(1)—Tl—O(2)	175·7 (3)		C(41)—P(2)—C(61)	108·1 (6)
O(1)—P(1)—C(11)	112·5 (6)		C(51)—P(2)—C(61)	106·6 (7)

H-atom positions were included in structure-factor calculation with B_{iso} fixed at 4·0 Å^2, but not refined. More details of the intensity data collection, structure solution and refinement are listed in Table 1. Final atomic coordinates are given in Table 2,

selected distances and angles in Table 3.* A *SCHAKAL* (Keller, 1988) plot of the molecule is shown in Fig. 1, and a stereoscopic view in Fig. 2.

Related literature. The structure of the title compound has been determined as one of a series of studies of complexes of thallium(III) halides with O-donor ligands (Bermejo, Castiñeiras, Gayoso, Hiller, Englert & Strähle, 1984; Hiller, García-Fernández, Bermejo & Castaño, 1986; Hiller, Castiñeiras, García-Fernández, Bermejo, Bravo & Sanchez, 1988; Castiñeiras, Hiller, Strähle, Bermejo & García-Vázquez, 1991), and is isotypic with TlBr$_3$(tppo)$_2$ (Jeffs, Small & Worrall, 1984), TlBrI$_2$(tppo)$_2$ (Castiñeiras, Hiller, Strähle, Bermejo & Gayoso, 1986), TlBr$_2$I(tppo)$_2$ (Castiñeiras, Hiller, Bermejo & Gayoso, 1986) and TlBrClI(tppo)$_2$ (Bermejo, Fernández, Gayoso, Castiñeiras, Hiller & Strähle, 1988).

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* Lists of structure factors, H-atom positions, bond distances and angles, torsion angles, least-squares planes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54025 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure du (Méthyl-4 pipérazinyl-1)-10 Pyrido[4,3-*b*][1,4]benzothiazépine

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Abstract. C$_{17}$H$_{18}$N$_4$S, $M_r = 310 \cdot 4$, monoclinic, $P2_1/n$, $a = 9 \cdot 171$ (3), $b = 9 \cdot 426$ (3), $c = 18 \cdot 476$ (5) Å, $\beta = 92 \cdot 20$ (3)°, $V = 1595 \cdot 9$ (1) Å^3, $Z = 4$, $D_x = 1 \cdot 292$ Mg m^{-3}, m.p. 416–417 K, λ(Mo $K\bar{\alpha}$) = $0 \cdot 7107$ Å, $\mu = 0 \cdot 164$ mm^{-1}, $F(000) = 660$, $T = 294$ (1) K, $R = 0 \cdot 067$ for 2314 independent reflections. The thiazepine ring is in a boat conformation while the piperazine ring is in the normal chair conformation. The dihedral angle between the two aromatic rings is $110 \cdot 5$ (1)°. The distances between the N(methyl) atom and the centres of the two aromatic rings are $6 \cdot 056$ (4) and $7 \cdot 726$ (4) Å, respectively. There are no hydrogen bonds.

Partie expérimentale. Cristal du composé (1) incolore $0,4 \times 0,4 \times 0,2$ mm obtenu par cristallisation dans un mélange méthanol(50% en volume)–acétone. Diffractomètre Siemens.

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