

envelope conformation as shown by the small O(1)-N(1)C(1)N(2) torsion angle of $-1.4(3)^\circ$. Within the ring, angles about vertex atoms C(1) and N(2) of 114.4 and 104.7° are significantly smaller than expected for sp^2 and sp^3 hybridized atoms. This may be due to steric factors in that methyl-group atoms C(6) and C(7) have close contact distances of 3.14 and 3.15 \AA to the semi-coordinated O(2) atom, or to ring conformation.

The aromatic ring of the ligand is almost exactly planar, the six atoms having mean and maximum distances of 0.002 and 0.004 \AA from the best least-squares plane through them. The oxide and amine atoms O(1) and N(2) lie 0.008 and 0.27 \AA on one side of the ring plane, and the ring is inclined to the coordination plane by 24.5° . Bonding distances and angles within the ring are essentially the same as those found in other complexes containing the pyridine *N*-oxide moiety (Estes & Hodgson, 1976; Al-Karaghoulí & Wood, 1979).

The perchlorate group is approximately tetrahedral with average bond length and angle values of $1.427(12) \text{ \AA}$ and $109.5(7)^\circ$. Its distortion may be attributed to interaction with Cu, and is best evidenced by the semi-coordinated O(2) having the longest Cl—O bond of $1.441(2) \text{ \AA}$. Apparently the ClO_4^- groups may

assume other bonding roles in this compound under slightly different conditions, since significant changes are observed in ClO_4^- IR frequencies after sample preparation by grinding or pressing techniques (West, 1978).

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Trichlorobis(4-pyridinecarbonitrile 1-oxide-O)thallium

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Abstract. $[\text{Tl}(\text{C}_6\text{H}_4\text{N}_2\text{O})_2\text{Cl}_3]$, $\text{C}_{12}\text{H}_8\text{Cl}_3\text{N}_4\text{O}_2\text{Tl}$, $M_r = 550.95$, monoclinic, C_c , $a = 7.0295(5)$, $b = 26.887(8)$, $c = 8.8436(8) \text{ \AA}$, $\beta = 105.85(5)^\circ$, $Z = 4$, $D_c = 2.28 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 10.66 \text{ mm}^{-1}$. The crystal consists of individual molecules held together by van der Waals contacts. The Tl atom is at the center of a distorted trigonal bipyramid, with the three Cl atoms in equatorial positions and the O atoms axial. The coordination appears new for Tl, its geometry being: Tl—Cl = $2.364(5)$ – $2.452(4) \text{ \AA}$, Tl—O = $2.36(1)$, $2.40(1) \text{ \AA}$, Cl—Tl—Cl = $140.2(2)$, $112.9(2)$, $106.6(2)^\circ$ and O—Tl—O = $168.9(5)^\circ$.

Introduction. Some attempts have been made to elucidate the stereochemistries of Tl trihalide complexes with donor molecules by spectroscopic techniques (Walton, 1968). Five different structural models have been proposed. However, evidence from X-ray diffraction has only been obtained for the compound TlCl_3 -(1,10-phenanthroline) (Baxter & Gafner, 1972). In the present paper, the structure of the complex of TlCl_3 with $\text{C}_6\text{H}_4\text{N}_2\text{O}$ is reported.

Samples were provided by Departamento de Química Inorgánica from the University of Santiago de Compostela (Spain). A pale-yellow prismatic crystal $0.26 \times 0.13 \times 0.08 \text{ mm}$ was used to collect the data. 3055 reflexions were measured in the $\omega/2\theta$ scan mode on a PW 1100 four-circle diffractometer, with graphite-

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monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). 2515 reflexions for which $I < 2\sigma(I)$ were considered as unobserved.

The systematic absences were hkl for $h + k$ odd, $h0l$ for l odd (h odd) and $0k0$ for k odd. The two possible space groups are Cc and $C2/c$. The intensities were corrected for absorption by *ORABS* (Schwarzenbach, 1972). Lorentz and polarization corrections were also applied. Scattering factors for neutral atoms were from *International Tables for X-ray Crystallography* (1974). Anomalous-dispersion factors were from Cromer & Liberman (1970).

The non-centrosymmetric space group Cc was chosen from the statistical distribution of intensities. Confirmation was obtained in the course of the struc-

Table 1. *Weighting scheme applied in the refinement*

$w = K/\sigma^2$	$K = 0.6210$	$\sigma = a + b F_o $
a	b	
5.4335	-0.0907	$35 > F_o$
2.3923	0.0007	$62 > F_o > 35$
0.1456	0.0369	$F_o > 62$

Table 2. *Final atomic coordinates for $Tl(C_6H_4N_2O)_2Cl_3$*

For Tl the values are given $\times 10^5$, for Cl $\times 10^4$, for H $\times 10^3$. For the remaining atoms x and z are shown $\times 10^3$, $y \times 10^4$. E.s.d.'s are in parentheses.

	x	y	z
Tl	0	60852 (1)	25000
Cl(1)	860 (6)	5392 (1)	4363 (5)
Cl(2)	-1015 (6)	6941 (1)	2403 (6)
Cl(3)	590 (8)	5907 (2)	50 (6)
O(1)	-329 (2)	5795 (4)	178 (2)
O(11)	336 (2)	6320 (4)	372 (1)
N(1)	-367 (2)	5325 (4)	199 (2)
N(11)	378 (2)	6767 (5)	324 (2)
N(2)	-514 (5)	3438 (7)	299 (3)
N(12)	465 (5)	8547 (6)	90 (3)
C(1)	-268 (2)	4964 (6)	148 (2)
C(2)	-309 (3)	4472 (6)	171 (2)
C(3)	-447 (3)	4351 (6)	246 (2)
C(4)	-482 (7)	3837 (6)	272 (4)
C(5)	-552 (2)	4729 (6)	294 (2)
C(6)	-494 (4)	5220 (5)	275 (2)
C(11)	392 (3)	7158 (6)	411 (2)
C(12)	419 (3)	7642 (6)	362 (2)
C(13)	432 (3)	7676 (6)	209 (2)
C(14)	452 (4)	8166 (7)	145 (3)
C(15)	426 (3)	7273 (6)	112 (2)
C(16)	405 (3)	6819 (7)	174 (2)
H(1)	-169	505	71
H(11)	378	713	520
H(2)	-231	420	125
H(12)	423	793	431
H(5)	-680	467	325
H(15)	452	731	-6
H(6)	-558	550	304
H(16)	409	651	110

ture solution. The heavy atom was located from the Patterson function. The positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses and refined by anisotropic full-matrix least squares. The H atom positions were calculated and included, but not varied. The weighting scheme applied by *PESOS* (Martinez-Ripoll & Cano, 1975) is given in Table 1. The final $R = 0.050$ and $R_w = 0.051$ for observed reflexions only, where $R_w = (\sum w\Delta^2 F / \sum w|F_o|^2)^{1/2}$. The final atomic parameters are listed in Table 2.*

Discussion. The structure consists of individual molecules of $Tl(C_6H_4N_2O)_2Cl_3$, Fig. 1. The Tl atom is at the center of a distorted trigonal bipyramid. This is the first complex of the type $TlCl_3L_2$ for which this coordination polyhedron has been found although it was proposed (Walton, 1968) for some related compounds. The two O atoms occupy the axial positions whereas the equatorial positions are occupied by the Cl atoms. The two pyridine rings are *trans* with respect to the line joining O(1) and O(11) and are twisted (40.3°) with respect to each other. The Tl atom deviates $0.073(2) \text{ \AA}$ from the plane through the three Cl atoms. The torsion angle N(1)—O(1)—O(11)—N(11) (12.57°) can be visualized in Fig. 2. Interatomic distances and angles are listed in Table 3. The bond lengths and angles are as expected for pyridine rings. The Tl—Cl lengths are similar to those found for terminal Tl—Cl bonds in $Tl(Cl_3)(phen)$ (Baxter & Gafner, 1972).

The distortion of the coordination polyhedron around the Tl atom can be described by the lack of linearity of the two Tl—O bonds [O—Tl—O angle,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34767 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

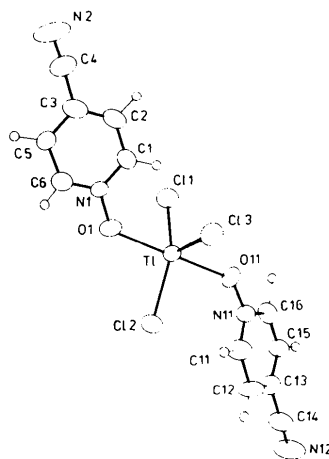


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule. The numbering corresponds to that in Table 2.

Table 3. Bond lengths (Å) and angles (°) for $\text{Tl}(\text{C}_6\text{H}_4\text{N}_2\text{O})_2\text{Cl}_3$

E.s.d.'s of values involving C and N are 0.03 Å and 2°.

Tl—Cl(1)	2.452 (4)	Cl(1)—Tl—Cl(2)	140.2 (2)
—Cl(2)	2.403 (4)	Cl(1)—Tl—Cl(3)	112.9 (2)
—Cl(3)	2.364 (5)	Cl(2)—Tl—Cl(3)	106.6 (2)
—O(1)	2.36 (1)	Cl(1)—Tl—O(1)	88.4 (3)
—O(11)	2.40 (1)	Cl(1)—Tl—O(11)	82.3 (3)
		Cl(2)—Tl—O(1)	92.7 (3)
		Cl(2)—Tl—O(11)	90.6 (3)
		Cl(3)—Tl—O(1)	95.2 (4)
		Cl(3)—Tl—O(11)	93.9 (3)
		O(1)—Tl—O(11)	168.9 (5)
		Tl—O(1)—N(1)	120.1 (9)
		Tl—O(11)—N(11)	111.5 (9)
	$x=0$ $x=1$	$x=0$ $x=1$	
N(x1)—O(x1)	1.31 1.34	O(x1)—N(x1)—C(x1)	120 122
C(x1)	1.34 1.29	O(x1)—N(x1)—C(x6)	119 120
C(x6)	1.29 1.40	C(x1)—N(x1)—C(x6)	121 118
C(x1)—C(x2)	1.38 1.40	N(x1)—C(x1)—C(x2)	120 125
C(x3)—C(x2)	1.36 1.38	C(x1)—C(x2)—C(x3)	120 115
C(x4)	1.43 1.46	C(x2)—C(x3)—C(x4)	119 119
C(x5)	1.39 1.38	C(x4)—C(x3)—C(x5)	122 117
C(x5)—C(x6)	1.40 1.36	C(x3)—C(x5)—C(x6)	117 116
N(x2)—C(x4)	1.13 1.15	N(x1)—C(x6)—C(x5)	122 122
		C(x2)—C(x3)—C(x5)	119 124
		N(x2)—C(x4)—C(x3)	177 178

168.9 (5)°] and by the difference in Tl—Cl lengths and Cl—Tl—Cl angles. Packing effects are probably responsible for the distortion. As can be seen in Fig. 2, the two Tl—O bonds bend toward the line through Cl(1) and Cl(2) and are a little nearer Cl(1). This is consistent with the opening of the Cl(1)—Tl—Cl(2) angle and with the elongation of the Tl—Cl(1) and Tl—Cl(2) bonds

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Bis(tetraphenylarsonium) Tris(2,2-diselenido-1,1-ethylenedicarbonitrile-*Se,Se'*)nickelate(IV)

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Abstract. $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Ni}\{\text{Se}_2\text{C}=\text{C}(\text{CN})_2\}_3]$, $2\text{C}_{24}\text{H}_{20}\text{As}^+\cdot\text{C}_{12}\text{N}_6\text{NiSe}_6^{2-}$, triclinic, $P\bar{1}$, $a = 14.434$ (2), $b = 14.567$ (2), $c = 16.869$ (2) Å, $\alpha = 105.48$ (1), $\beta = 101.90$ (1), $\gamma = 113.42$ (1)°, $D_o = 1.72$ (1), $Z = 2$, $D_c = 1.729$ Mg m⁻³; $R = 0.054$ for 3643 reflexions with $I > 3\sigma(I)$. The six Se atoms surround the Ni atom in a distorted octahedral coordination. Some average distances are Ni—Se 2.387 (1), Se—Se (intraligand)

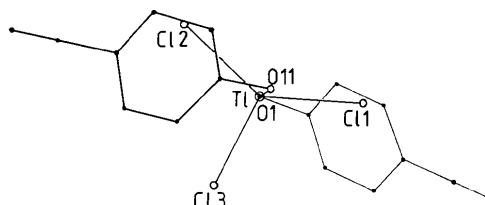


Fig. 2. Projection of the molecule on the equatorial plane showing the distortion of the coordination polyhedron around the Tl atom.

with respect to the other Tl—Cl bond. Another feature which could also be attributed to packing effects is the difference in the Tl—O(1)—N(1) and Tl—O(11)—N(11) angles (120.1 and 111.5°, respectively).

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