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Structure of the 4:1 Complexes Formed by Pyridine and the Group III Halides $InCl_3$ and $TlCl_3$: *mer*-Trichlorotris(pyridine)indium(III)–pyridine (1/1), $[InCl_3(C_5H_5N)_3].C_5H_5N$, and *mer*-Trichlorotris(pyridine)thallium(III)–pyridine (1/1), $[TlCl_3(C_5H_5N)_3].C_5H_5N$

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Abstract. $[InCl_3(C_5H_5N)_3].C_5H_5N$: $M_r = 537{\cdot}4$, orthorhombic, $C222_1$, $a = 9{\cdot}117\,(7)$, $b = 16{\cdot}83\,(2)$, $c = 14{\cdot}66\,(1)$ Å, $V = 2250\,(5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}59$, $D_x = 1{\cdot}586$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7106$ Å, $\mu = 1{\cdot}30$ mm^{-1}, $F(000) = 1072$, room temperature, $R = 0{\cdot}050$ for 1260 measured intensities. $[TlCl_3(C_5H_5N)_3].C_5H_5N$: $M_r = 627{\cdot}0$, orthorhombic, $C222_1$, $a = 9{\cdot}040\,(7)$, $b = 16{\cdot}88\,(2)$, $c = 14{\cdot}75\,(1)$ Å, $V = 2250\,(7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}94$, $D_x = 1{\cdot}851$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7106$ Å, $\mu = 7{\cdot}23$ mm^{-1}, $F(000) = 1200$, room temperature, $R = 0{\cdot}061$ for 1379 measured intensities. The crystal structures are isomorphous and consist of 'octahedral' $MCl_3(C_5H_5N)_3$ molecules with *mer* geometry and an additional pyridine molecule of crystallization. The molecules have C_2 symmetry. The bond distances and angles in the pyridine rings are normal as are the coordination bond lengths. There is angular distortion of the complex due to repulsion by the Cl atom *trans* to one of the coordinated pyridines.

Introduction. There are only a few examples of indium and thallium trihalide complexes with stoichiometry $MX_3.4L$ (L is a monodentate ligand). $InBr_3.4C_5H_5N$ consists of 'octahedral' $InBr_3.3C_5H_5N$ molecules with one uncoordinated pyridine (Small & Worrall, 1982) and the compounds $TlX_3.4H_2O$ (X = Cl, Br) consist of trigonal bipyramidal $TlX_3.2H_2O$ with two lattice water molecules (Glaser, 1979). We here report the structures of two new complexes prepared by us, $InCl_3.4C_5H_5N$ and $TlCl_3.4C_5H_5N$.

Experimental. $TlCl_3.4C_5H_5N$ prepared by adding excess dry pyridine to solution of Tl^{III} chloride in acetonitrile. Suitable crystals obtained by recrystallizing from pyridine. $InCl_3.4C_5H_5N$ prepared by dissolving In^{III} chloride in dry pyridine. The solution was concentrated and suitable crystals slowly formed. In both cases crystals transferred to Lindemann tubes in nitrogen-filled dry box. Crystal data obtained from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å); D_m measured by flotation in benzene/methylene dibromide solutions. Intensity measurements made on Stoe STADI-2 two-circle automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation; layers $k = 0$–16 In (0–14 Tl) measured; $2\theta < 50°$; crystal size $0{\cdot}33 \times 0{\cdot}33 \times 0{\cdot}11$ mm ($0{\cdot}19 \times 0{\cdot}09 \times 0{\cdot}19$ mm). Absorption corrections (max. and min.) 0·75, 0·48 (0·31, 0·16) and scaling of data carried out with *SHELX*76 (Sheldrick, 1976). 1629 (1388) reflections measured; elimination of those with $I < 3\sigma(I)$ gave 1260 (1379) unique reflections. Standards measured every 10 reflections: variation 1%. Same programs used for all other calculations. In and Tl atom positions, obtained from Patterson maps, used to phase $(F_o - F_c)$ maps to give positions of remaining atoms (apart from hydrogen). Unit weights, full-matrix least-squares refinement (on F) of all atomic positions, anisotropic U_{ij} values for In(Tl) and Cl, isotropic U values for remaining non-H atoms, convergence at $R = 0{\cdot}050$ (0·061). In each case the enantiomorph was also refined and increased R slightly. In Tables 1 and 2 it can be seen that enantiomorphs of opposite hands were used. Max. Δ/σ 0·164 (0·150); max. in final difference Fourier map 1·01 e Å^{-3} (3·08 e Å^{-3}, associated mainly with Tl). No correction for secondary extinction. Atomic scattering factors those of Cromer & Mann (1968) and Cromer & Liberman (1970).

Discussion. Final coordinates and equivalent isotropic thermal parameters (U_{eq}) for In, Tl and Br, and isotropic thermal parameters for C and N are given in Tables 1 and 2.* The crystal structures are isomorphous and consist of 'octahedral' neutral molecules $MCl_3.3C_5H_5N$ with *mer* (*trans*) geometry and additional pyridine molecules of crystallization (Figs. 1 and 2) and are similar to the $InBr_3$ analogue (Small & Worrall, 1982). The molecules have twofold symmetry (C_2) with Cl(1), M, N(1) and C(1) occupying special positions on the twofold (rotation) axis. The interplane angle of the

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39409 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* (×10⁴), *equivalent isotropic thermal parameters for indium and chlorine and isotropic thermal parameters for carbon and nitrogen* (Å² × 10⁴)

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i a_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
In	0*	8353 (1)	7500*	289 (15)
Cl(1)	0*	9822 (5)	7500*	442 (30)
Cl(2)	2714 (3)	8303 (2)	7536 (5)	436 (22)
N(1)	0*	6941 (12)	7500*	266 (29)
N(2)	110 (17)	8295 (5)	5933 (5)	321 (21)
N(3)	5857 (34)	0*	0*	1257 (106)
C(1)	0*	5313 (14)	7500*	437 (47)
C(2)	8699 (19)	5716 (10)	7733 (11)	650 (50)
C(3)	8761 (15)	6525 (9)	7713 (8)	496 (37)
C(4)	980 (18)	8784 (10)	5493 (10)	502 (39)
C(5)	1066 (20)	8810 (11)	4503 (11)	594 (45)
C(6)	232 (17)	8286 (9)	4034 (8)	484 (37)
C(7)	9267 (21)	7747 (12)	4475 (12)	638 (49)
C(8)	9235 (17)	7786 (10)	5473 (10)	464 (36)
C(9)	2833 (39)	0*	0*	1070 (109)
C(10)	3542 (31)	9380 (17)	9542 (19)	1190 (94)
C(11)	5203 (34)	9418 (12)	9581 (14)	960 (71)

* Constrained.

Table 2. *Fractional atomic coordinates* (×10⁴), *equivalent isotropic thermal parameters for thallium and chlorine and isotropic thermal parameters for carbon and nitrogen* (Å² × 10⁴)

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i a_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Tl	0*	1627 (1)	2500*	333 (5)
Cl(1)	0*	134 (4)	2500*	467 (30)
Cl(2)	7240 (4)	1701 (4)	2476 (7)	560 (28)
N(1)	0*	3097 (9)	2500*	180 (27)
N(2)	−137 (23)	1696 (8)	4109 (8)	325 (31)
N(3)	−5826 (60)	0*	0*	981 (157)
C(1)	0*	4682 (19)	2500*	645 (77)
C(2)	1249 (34)	4300 (19)	2269 (20)	807 (95)
C(3)	1232 (28)	3493 (16)	2303 (18)	666 (74)
C(4)	−964 (28)	1244 (15)	4539 (16)	528 (57)
C(5)	−1041 (34)	1192 (18)	5501 (19)	701 (74)
C(6)	−223 (34)	1718 (14)	5962 (15)	587 (64)
C(7)	679 (32)	2241 (18)	5529 (19)	669 (73)
C(8)	715 (28)	2205 (16)	4578 (16)	542 (58)
C(9)	−2854 (70)	0*	0*	1174 (197)
C(10)	−3552 (48)	629 (28)	425 (29)	1167 (139)
C(11)	−5242 (49)	586 (19)	413 (22)	931 (104)

* Constrained.

Table 3. *Bond distances* (Å) *and angles* (°) *for* $InCl_3.4C_5H_5N$

In—Cl(1)	2·471 (8)	In—Cl(2)	2·476 (2)
In—N(1)	2·377 (21)	In—N(2)	2·302 (7)
C(1)—C(2)	1·41 (2)	C(2)—C(3)	1·36 (2)
N(1)—C(3)	1·36 (2)	C(4)—C(5)	1·45 (2)
C(4)—N(2)	1·31 (2)	C(5)—C(6)	1·35 (2)
C(6)—C(7)	1·42 (2)	C(7)—C(8)	1·47 (2)
N(2)—C(8)	1·35 (2)	N(3)—C(11)	1·30 (2)
C(9)—C(10)	1·40 (3)	C(10)—C(11)	1·52 (4)
Cl(1)—In—Cl(2)	92·0 (1)	N(1)—In—Cl(2)	88·0 (1)
N(2)—In—Cl(1)	92·5 (2)	N(1)—In—N(2)	87·5 (2)
N(2)—In—Cl(2)	88·6 (4)	N(2)—In—N(2^{i})	175·1 (2)
N(1)—In—Cl(1)	180·0		

Symmetry code: (i) $-x, y, \tfrac{1}{2} - z$.

Table 4. *Bond distances* (Å) *and angles* (°) *for* $TlCl_3.4C_5H_5N$

Tl—Cl(1)	2·520 (6)	Tl—Cl(2)	2·498 (4)
Tl—N(1)	2·482 (15)	Tl—N(2)	2·380 (12)
C(1)—C(2)	1·34 (3)	C(2)—C(3)	1·36 (4)
N(1)—C(3)	1·33 (3)	C(4)—C(5)	1·42 (3)
C(4)—N(2)	1·24 (3)	C(5)—C(6)	1·34 (4)
C(6)—C(7)	1·36 (4)	C(7)—C(8)	1·41 (3)
N(2)—C(8)	1·35 (3)	N(3)—C(11)	1·28 (4)
C(9)—C(10)	1·38 (5)	C(10)—C(11)	1·53 (6)
Cl(1)—Tl—Cl(2)	92·9 (1)	N(1)—Tl—Cl(2)	87·1 (1)
N(2)—Tl—Cl(1)	92·8 (3)	N(1)—Tl—N(2)	87·2 (3)
N(2)—Tl—Cl(2)	87·7 (4)	N(2)—Tl—N(2^{i})	174·4 (3)
N(1)—Tl—Cl(1)	180·0		

Symmetry code: (i) $-x, y, \tfrac{1}{2} - z$.

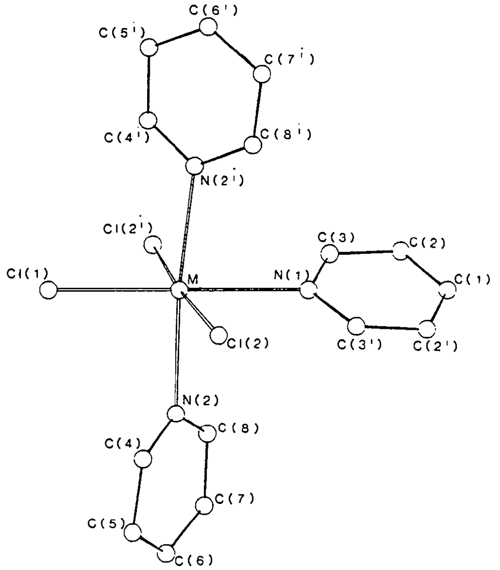

Fig. 1. Structure of MCl$_3$.3C$_5$H$_5$N (M = In, Tl).

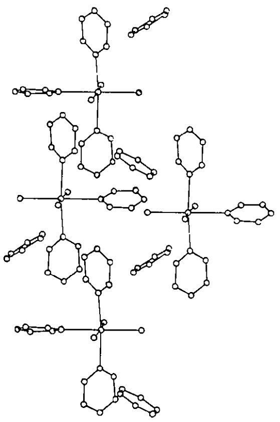

Fig. 2. Position of pyridine solvate molecules within the crystal.

trans pyridines [rings containing N(2) and N(2^{i})] is 90 (3)° and these planes are at 45 (3)° to the *M*—Cl and *M*—N directions in the intermediate plane. The *mer* geometry of the indium complex was not predicted by previous vibrational spectroscopic studies (Carty & Tuck, 1975); this has been discussed by us recently (Small & Worrall, 1982).

Bond distances and angles are listed in Tables 3 and 4; the In—N distance, 2·33 (2) Å (av), is almost equal to that observed in the analogous bromide complex, suggesting that the acceptor strengths of the halides are similar with respect to pyridine. The In—Cl distance, 2·474 (4) Å (av), compares with 2·524 (5) Å (av) observed in $InCl_6^{3-}$ (Contreras, Einstein, Gilbert & Tuck, 1977). The Tl—Cl bond lengths, 2·505 (5) Å (av), are similar to those in other six-coordinate Tl compounds [2·48–2·54 Å (Lee, 1971)] as are the Tl—N distances, 2·41 (1) Å, compared with 2·44 (2) Å in $TlBr_3$.2pyridine (Jeffs, Small & Worrall, 1984) and 2·36 (2) Å in $TlCl_3$.(1,10-phenanthroline) (Baxter & Gafner, 1972). The main angular distortions are due to repulsions by Cl(1) which lies *trans* to N(1). The large *U* values are to be expected for the unbound pyridine.

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Structure of Semiconducting 3,4;3′,4′-Bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene–Hexafluoroarsenate (2:1), $(BEDT\text{-}TTF)_2AsF_6$, $(C_{10}H_8S_8)_2AsF_6$

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Abstract. $M_r = 958{\cdot}287$, monoclinic, $A2/a$, $a = 14{\cdot}890\ (12)$, $b = 6{\cdot}666\ (7)$, $c = 35{\cdot}3789\ (12)$ Å, $\beta = 111{\cdot}19\ (10)$°, $V = 3274$ Å^3, $Z = 4$, $D_x = 1{\cdot}94$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å) $= 2{\cdot}07$ mm^{-1}, $F(000) = 1916$, $T = 298$ K, $R(F) = 0{\cdot}055$ for 1323 observed reflections. The structure consists of two-dimensional sheets of BEDT-TTF ($C_{10}S_8H_8$) molecules separated by AsF_6^- anions. Short S—S contact distances are found normal to the molecular stacks but not along the stacking direction. The material undergoes a low-temperature (*a*, 2*b*, *c*) phase transition above 125 K.

Introduction. A new family of organic conductors has recently been synthesized, namely, the charge-transfer salts of 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene (BEDT-TTF): *e.g.* $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0\cdot5}$ (Saito, Enoki, Toriumi & Inokuchi, 1982). These include the first sulfur-based organic superconductor $(BEDT\text{-}TTF)_2ReO_4$, $T_c = 2$ K at 0·4 G Pa pressure (Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983). Crystals of these materials contain segregated stacks of donor and acceptor molecules with significant intermolecular S···S interactions between the organic molecules normal to the stacking direction (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito & Inokuchi, 1983; Kobayashi, Mori, Kato, Kobayashi, Sasaki, Saito & Inokuchi, 1983; Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983) and as

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