Synthesis, Spectroscopic, and Structural[*] Studies of Dimethylthallium(III) Complexes containing Heterocyclic Nitrogen-donor Ligands, including '$TlC_2N_3O_2$' and 'TlC_2O_6' Geometries

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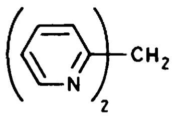
The complexes dimethyl[2-(pyridin-2-yl)imidazolato]thallium(III), (2,2′-bi-imidazolato)bis[dimethylthallium(III)], and their benzimidazolato-analogues are monomeric in chloroform. Dimethylthallium(III) nitrate forms complexes of stoicheiometry $[TlMe_2L]NO_3$ {L = 1,10-phenanthroline, 4,4′-diethyl-2,2′-bipyridyl, *N*-methyl-2-(pyridin-2-yl)imidazole (pymim), bis(pyridin-2-yl)methane [$(py)_2CH_2$], or bis(*N*-methylimidazol-2-yl)methanol [$(mim)_2CHOH$]}, $[TlMe_2(terpy)]NO_3 \cdot H_2O$ (terpy = 2,2′:6′,2″-terpyridyl), and $[(TlMe_2)_3(Et_3terpy)_2][NO_3]_3$ (Et_3terpy = 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl). Proton n.m.r. spectra of the nitrate complexes in methanol indicate co-ordination of the nitrogen-donor ligands to the dimethylthallium(III) cation. The structures of the $(py)_2CH_2$, terpy, and Et_3terpy complexes have been determined by single-crystal *X*-ray diffraction at 295 K and refined by least-squares methods to *R* 0.048, 0.061, and 0.071 for 2 739, 3 000, and 1 547 independent 'observed' reflections, respectively. The complexes have linear or slightly bent C–Tl–C groups, with weak Tl··· N and/or Tl··· O interactions in approximate equatorial planes. The $(py)_2CH_2$ complex has a dimeric, centrosymmetric, structure with nitrate groups weakly linking two '$TlMe_2\{(py)_2CH_2\}$' groups to form $[\{TlMe_2[(py)_2CH_2](NO_3)\}_2]$ with '$TlC_2N_2O_3$' co-ordination having Tl··· N 2.658(9) and 2.666(9), Tl··· O 2.770(9)—2.915(10) Å, and C–Tl–C 171.7(5)°, opposite $(py)_2CH_2$. The terpy complex has a tridentate ligand [Tl··· N 2.620(10)—2.650(9) Å] with a water molecule and nitrate ion 2.932(12) and 3.250(19) Å from thallium, and is thus formulated as $[TlMe_2(terpy)(H_2O)]NO_3$, with a '$TlC_2N_3O_2$' environment having C–Tl–C 169.6(6)° opposite terpy. The Et_3terpy complex has two '$TlMe_2(Et_3terpy)$' groups [C–Tl–C 166(1)° opposite tridentate Et_3terpy, Tl··· N 2.61(3)—2.66(3) Å] linked by a '$TlMe_2(NO_3)_3$' group [linear C–Tl–C, Tl··· O 2.72(2)—2.85(3) Å] to give the molecule $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$ possessing a two-fold axis and '$TlC_2N_3O_2$' and 'TlC_2O_6' co-ordination environments. Crystal data: $[\{TlMe_2[(py)_2CH_2](NO_3)\}_2]$ monoclinic, space group $P2_1/c$, a = 8.923(3), b = 22.535(8), c = 7.527(3) Å, β = 96.78(3)°, and Z = 2; $[TlMe_2(terpy)(H_2O)]NO_3$ monoclinic, space group $P2_1/c$, a = 9.779(3), b = 13.290(3), c = 14.380(4) Å, β = 93.95(2)°, and Z = 4; $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$ tetragonal, space group $I4_1/a$, a = 15.715(6), c = 45.21(1) Å, and Z = 8.

Crystallographic studies of the interaction of dimethylthallium(III) with neutral donor ligands have revealed novel stereochemistries.[1–4] For the four complexes studied to date the $[TlMe_2]^+$ moiety is linear in crown ether complexes [178(1), 177.5(4), or 180°],[2–4] with the environment 'TlC_2O_6' involving weak Tl··· O interactions [2.694(10)—2.979(5) Å] in the equatorial region,[2–4] or slightly bent in $[TlMe_2(phen)]ClO_4$ with the environment '$TlC_2N_2O_2$' involving Tl··· N [2.57(3) Å] and Tl··· O [2.88(3) Å] in the equatorial region and the C–Tl–C angle [168(1)°] opposite the stronger thallium–1,10-phenanthroline interaction.[1]

As 1,10-phenanthroline is a rigid ligand, and the cyclic crown ethers are expected to favour strongly formation of six Tl··· O interactions, we have explored the interaction of $[TlMe_2]^+$ with ligands possessing more flexibility in their co-ordination behaviour. Thus, bis(pyridin-2-yl)methane [$(py)_2CH_2$] and bis(*N*-methylimidazol-2-yl)methanol [$(mim)_2CHOH$] possess flexibility about the bridging carbon atom, and the ligands *N*-methyl-2-(pyridin-2-yl)imidazole (pymim), 4,4′-diethyl-2,2′-bipyridyl (Et_2bipy), 2,2′:6′,2″-terpyridyl (terpy), and 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl (Et_3terpy) are also expected to be flexible, *e.g.* Et_3terpy acts as a tridentate ligand to methylmercury(II) in the solid state but as a bidentate ligand in methanol,[5,6] and bidentate co-ordination of terpy in the solid state has been established crystallographically for $[Ru(CO)_2Br_2(terpy)]$.[6][†]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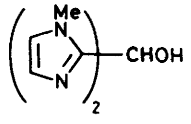
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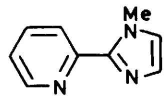
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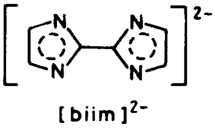
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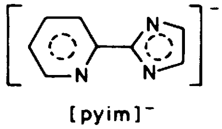
$[pyim]^-$

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[*] *Supplementary data available* (No. SUP 56469, 16 pp.): thermal parameters, H-atom parameters, ligand bond distances and angles, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

[†] For other examples involving the proposal that terpy acts as a bidentate ligand, largely from spectroscopic data, see refs. 5 and 7.

Table 1. Characterisation data for the complexes

	Analysis (%)[a]			$\nu_{asym}(TlC_2)$[b]/ cm^{-1}	^{1}H N.m.r.[c]		
Complex stoicheiometry	C	H	N		$\delta(TlMe_2)$	$\lvert ^2J(^1H-Tl)\rvert$[d]	Ligand[e]
$[TlMe_2(phen)]NO_3$	35.7 (35.3)	2.8 (3.0)	8.4 (8.8)	550	1.04	420.8	9.17, **2**, *dd*, H(2,9); 8.63, **2**, *dd*, H(4,7); 8.06, **1**, *s*, H(5,6); 7.94, **2**, *m*, H(3,8)[f]
$[TlMe_2(Et_2bipy)]NO_3$	37.6 (37.8)	3.9 (4.4)	8.2 (8.3)	548	1.01	420.4	8.57, **2**, *d*, H(6); 8.17, **2**, *s*, H(3); 7.38, **2**, *d*, H(5); 2.81, **4**, *q*, CH_2; 1.33, **6**, *t*, CH_3[g]
$[TlMe_2(pymim)]NO_3$	28.9 (29.0)	3.1 (3.3)	12.3 (12.3)	550	1.28	421.6	8.88, **1**, *d*, H(6); 8.22—8.11, **2**, *m*, H(3,4); 7.63, **1**, *m*, H(5); 7.46, **1**, *s*, and 7.31, **1**, *s*, H(4′,5′); 4.30, **3**, *s*, CH_3[h]
$[TlMe_2\{(py)_2CH_2\}]NO_3$	33.3 (33.5)	3.2 (3.5)	9.3 (9.0)	560	1.07	421.8	8.47, **2**, *d*, H(6); 7.78, **2**, *m*, H(4); 7.35, **2**, *d*, H(3); 7.29, **2**, *m*, H(5); 4.31, **2**, *s*, CH_2[i]
$[TlMe_2\{(mim)_2CHOH\}]NO_3$	26.9 (27.0)	3.6 (3.7)	14.5 (14.3)	552	1.03	420.7	7.10, **2**, *d*, and 6.90, **2**, *d*, H(4,5); 6.12, **1**, *s*, CHOH; 3.73, **6**, *s*, CH_3[j]
$[TlMe_2(terpy)]NO_3\cdot H_2O$	37.3 (37.3)	3.4 (3.5)	10.4 (10.2)	544	0.89	422.8	8.83, **2**, *d*, H(6,6″); 8.51—8.43, **4**, m, H(3,3′,5′,3″); 8.28, **1**, *m*, H(4′); 8.13, **2**, *m*, H(4,4″); 7.65, **2**, *m*, H(5,5″)[k]
$[(TlMe_2)_3(Et_3terpy)_2][NO_3]_3$	37.6 (37.8)	4.1 (4.2)	8.5 (8.3)	546	0.89	421.7	8.71, **2**, *d*, H(6,6″); 8.41, **2**, *s*, and 8.37, **2**, *s*, H(3′,5′, 3,3″); 7.56, **2**, *d*, H(5,5″); 3.00, **2**, *q*, CH'_2; 2.90, **4**, *q*, CH_2 and CH''_2; 1.46, **3**, *t*, CH'_3; 1.38, **6**, *t*, CH_3 and CH''_3[l]
$[TlMe_2(pyim)]$[m]	31.3 (31.7)	3.2 (3.2)	11.0 (11.1)	524	1.01	366.6	8.24, **1**, *d*, H(3); 8.18, **1**, *d*, H(6); 7.76, **1**, *m*, H(4); 7.18, **2**, *s*, im; 7.14, **1**, *m*, H(5)[n]
$[TlMe_2(pybzim)]$[m]	39.8 (39.2)	3.5 (3.3)	9.9 (9.8)	534	1.04	364.0	8.60, **1**, *d*, H(3); 8.30, **1**, *d*, H(6); 7.85, **1**, *m*, H(4); 7.69, **2**, *br*, H(3′,6′); 7.29, **1**, *m*, H(5); 7.17, **2**, *m*, H(4′,5′)[o]
$[(TlMe_2)_2biim]$[m]	19.9 (20.0)	2.5 (2.7)	9.2 (9.3)	536	0.99	371.2	6.92, **2**, *s*
$[(TlMe_2)_2bibzim]$[m]	30.9 (30.8)	2.4 (2.9)	8.2 (8.0)	528	1.12	365.9	7.59, **2**, *m*, H(3,6); 7.18, **2**, *m*, H(4,5)

[a] Calculated values are given in parentheses. [b] Nujol mulls, medium–weak absorption; $[TlMe_2]NO_3$ has ν_{asym} at 562w cm^{-1}. [c] Shifts in p.p.m. from $SiMe_4$ in CD_3OD (nitrate complexes) or $CDCl_3$ (other complexes); given as chemical shift, **relative intensity**, *multiplicity*; $[TlMe_2]NO_3$ has $\delta(TlMe_2)$ 1.05 and $\lvert ^2J(^1H-Tl)\rvert$ 422.5 Hz in methanol. [d] Broad resonances, with $\lvert ^2J(^1H-^{203}Tl)\rvert$ and $\lvert ^2J(^1H-^{205}Tl)\rvert$ not resolved (width at half-height *ca.* 20 Hz). [e] Spectra of free ligands in CD_3OD are given in footnotes (*f*—*l*) for ligands forming nitrate complexes. [f] $J(H^3,H^4) = 8.2$, $J(H^2,H^3) = 4.6$, and $J(H^2,H^4) = 1.5$ Hz. phen$\cdot H_2O$: 8.94, *dd*, H(2,9); 8.16, *dd*, H(4,7); 7.59, *s*, H(5,6); and 7.56, *m*, H(3,8); $J(H^3,H^4) = 8.1$, $J(H^2,H^3) = 4.4$, and $J(H^2,H^4) = 1.7$ Hz. [g] $J(H^5,H^6) = 5.1$, $J_{ethyl} = 7.6$ Hz. Et_2bipy: 8.50, *dd*, H(6,6′); 8.13, *s*, H(3,3′); 7.28, *d*, H(5,5′); 2.75, *q*, CH_2; and 1.30, *t*, CH_3; $J(H^5,H^6) = 5.1$, $J(H^4,H^6) = 1.5$, and $J_{ethyl} = 7.6$ Hz. [h] $J(H^5,H^6) = 4.8$. pymim: 8.59, *ddd*, H(6); 7.96, *m*, H(3); 7.83, *m*, H(3); 7.31, *m*, H(5); 7.17, *d*, and 7.06, *d*, H(4′,5′); and 4.02, *s*, CH_3; $J(H^5,H^6) = 4.8$, $J(H^4,H^6) = 1.6$, $J(H^3,H^6) = 0.9$, and $J(H^{4'}H^{5'}) = 1$ Hz. [i] $J(H^3,H^4) = 7.9$ and $J(H^5,H^6) = 4.3$ Hz. $(py)_2CH_2$: 8.46, *m*, H(6); 7.72, *m*, H(4); 7.32, *d*, H(3); 7.24, *m*, H(5); 4.31, *s*, CH_2; $J(H^5,H^6) \sim 4.5$, $J(H^3,H^4) = 7.9$ Hz. [j] $J(H^4,H^5) = 1$ Hz. $(mim)_2CHOH$: 7.10, *d*, and 6.90, *d*, H(4,5); 6.11, *s*, CHOH; and 3.75, *s*, CH_3; $J(H^4,H^5) = 1.2$ Hz. [k] $J(H^5,H^6) = 5$ Hz. terpy: 8.65, *m*, H(6,6″); 8.60, *m*, H(3,3″); 8.36, *d*, H(3′,5′); 8.02, *m*, H(4′); 7.97, *m*, H(4,4″); and 7.45, *m*, H(5,5″); $J(H^3,H^4)$ *ca.* 8.0, $J(H^{3'}H^{4'}) = 7.9$, and $J(H^5,H^6)$ *ca.* 4.8 Hz. [l] $J(H^5,H^6) = 5.1$ and $J(H^7,H^8) = 7.6$ Hz. Et_3terpy: 8.53, *d*, H(6,6″); 8.43, *s*, H(3,3″); 8.18, *s*, H(3′,5′); 7.34, *m*, H(5,5″); 2.86, *q*, (CH'_2); 2.82, *q*, (CH_2, CH''_2); 1.38, *t*, CH'_3; and 1.35, *t*, (CH_3, CH''_3); $J(H^5,H^6) = 5.0$ and $J_{ethyl} = 7.7$ Hz. [m] Molecular weights in chloroform at 37 °C determined by osmometry, with concentration and calculated value for monomer in parentheses: $[TlMe_2(pyim)]$, 382 (31.9, 379); $[TlMe_2(pybzim)]$, 413 (27.9, 429); $[(TlMe_2)_2biim]$, 613 (44, 601); and $[(TlMe_2)_2bibzim]$, 714 (36.4 mmol dm^{-3}, 701). [n] $J(H^3,H^4) = 8.2$ and $J(H^5,H^6) = 4.8$ Hz. [o] $J(H^3,H^4) = 8.1$ and $J(H^5,H^6) = 4.4$ Hz.

To complement these studies we have re-examined phen as a model bidentate ligand, and included more basic pyridine and imidazole donors derived by deprotonation of 2,2′-bi-imidazole (giving $[biim]^{2-}$), 2-(pyridin-2-yl)imidazole (giving $[pyim]^-$), and their benzimidazole analogues.

Results

Preparation and Characterisation of Complexes.—The nitrate complexes were obtained as colourless crystals on reaction of dimethylthallium(III) nitrate with an equimolar quantity of ligand in acetone to give products of stoicheiometry $[TlMe_2L]NO_3$, except for the terpy complex which crystallised as a monohydrate and the Et_3terpy complex which formed crystals of stoicheiometry $[(TlMe_2)_3(Et_3terpy)_2][NO_3]_3$.

The binuclear complexes $[(TlMe_2)_2L]$ [L = biim or 2,2′-bibenzimidazolate (bibzim)] were prepared by reaction of dimethylthallium(III) iodide with an alkaline solution of the ligands in water, and the complexes $[TlMe_2L]$ [L = pyim or 2-(pyridin-2-yl)benzimidazolate (pybzim)] were obtained on refluxing a suspension of the iodide with silver(I) derivatives of L in dichloromethane followed by separation of insoluble AgI.

The complexes have microanalysis and ^{1}H n.m.r. spectra consistent with the formulae presented, and the neutral complexes $[(TlMe_2)_2L]$ and $[TlMe_2L]$ are monomeric in chloroform (Table 1). The nitrate complexes exhibit $\nu_{asym}(TlC_2)$ at 560—544 cm^{-1}, slightly lower than for $[TlMe_2]NO_3$ (562 cm^{-1}), although similar to that for $[TlMe_2]ClO_4$ (555 cm^{-1});[8] binding to the more basic ligands present in the neutral complexes results in lowering of $\nu_{asym}(TlC_2)$ to 536—528 cm^{-1}. The nitrates have nitrate absorption(s) in the region 1 400—1 300 cm^{-1}, compared with intense and broad absorption at 1 450—1 300 cm^{-1} for $[TlMe_2]NO_3$, but the presence of ligand absorption in this region prevents precise assignment of nitrate absorption(s) for most of the complexes.

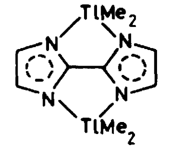
There appear to be no reports of stability-constant determinations for the interaction of dimethylthallium(III) with neutral donor ligands, although constants for some anionic ligands have been measured, *e.g.* log *K* 5.56 ± 0.01 for the 2,4-pentanedionato complex.[9] Co-ordination of neutral ligands to $[TlMe_2]^+$, when present in 1 : 1 mole ratio in solution, has been demonstrated for crown ethers[2,3,10] and nitrogen-donor macrocycles[11] by n.m.r. spectroscopy, and co-ordination by pyridine in acetonitrile is likely since $[TlMe_2(py)]ClO_4$ may be recrystallised from acetonitrile.[8]

If the complexes of neutral donor ligands reported here are partially or substantially dissociated in solution, $[TlMe_2]^+ + L \rightleftharpoons [TlMe_2L]^+$, then the ^1H n.m.r. resonances will be a result of averaging of the resonances for the species in solution. Thus, although $\delta(TlMe_2)$ and $|^2J(^1H-Tl)|$ are essentially unchanged from the values for $[TlMe_2]NO_3$ (Table 1), it is of interest that, except for $(mim)_2CHOH$, the ligand resonances are altered from the free-ligand values, indicating *at least* partial complex formation in methanol, *e.g.* downfield shifts of 0.23—0.47 and 0—0.06 p.p.m. occur for the phen and $(py)_2CH_2$ resonances, respectively, and both upfield (0.06 p.p.m.) and downfield (0.22—0.26 p.p.m.) shifts occur for Et_3terpy.

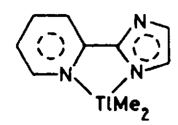
For the complexes of Et_2bipy, terpy, and Et_3terpy, changes in the chemical shift difference between H(3,3′) and H(5,5′) (Et_2bipy), and between H(3,3″), H(5,5″), and H(3′,5′) (terpy, Et_3terpy) are clearly indicative of interaction with $[TlMe_2]^+$. Differences between these resonances for 2,2′-bipyridyls are known to be sensitive to the interplanar angle between the pyridin-2-yl rings,[12,13] which alters on protonation,[13] and interaction with other electrophiles such as methylmercury(II)[14] and dichloroplatinum(II)[15] also induces changes in the chemical shift difference between H(3,3′) and H(5,5′). Thus, in the presence of $[TlMe_2]^+$ changes in these differences at least partly reflect changes in the interplanar angle(s) from values for the ligands in CD_3OD [*e.g.* 80—100° for 2,2′-bipyridyl(s)] to other values resulting on co-ordination to $[TlMe_2]^+$, *e.g.* for terpy $\Delta(3,3''-5,5'')$ alters from 1.09 to 0.81 p.p.m. and $\Delta(3,3''-3,5')$ from 0.25 to 0.04 p.p.m. on interaction with $[TlMe_2]^+$.

Although the ^1H n.m.r. spectra of the nitrate complexes indicate *co-ordination* of the ligands in methanol, the ligands are not necessarily *chelated* except for 1,10-phenanthroline, as they are flexible in their co-ordination behaviour.

For the nitrate complexes bonding between $[TlMe_2]^+$ and the ligands in solution is clearly weak as $\delta(TlMe_2)$ and $|^2J(^1H-Tl)|$ are essentially unaltered from the values for $[TlMe_2]^+$, in contrast to the neutral complexes of the deprotonated ligands, $[(TlMe_2)_2L]$ and $[TlMe_2L]$, for which a decrease of 50—60 Hz in $|^2J(^1H-Tl)|$ on co-ordination is indicative of much stronger Tl–N interactions. The coupling constants obtained, 364—371.2 Hz, are similar to those observed for related complexes of deprotonated pyrazoles, *e.g.* $[\{TlMe_2(\mu-C_3H_3N_2-N,N')\}_2]$ has $|^2J(^1H-Tl)|$ 376 Hz in C_6D_6.[16] Thus, the n.m.r. spectra of these complexes, and their monomeric behaviour in chloroform, are consistent with the structures shown, involving quadridentate $[biim]^{2-}$ and $[bibzim]^{2-}$ and bidentate $[pyim]^-$ and $[pybzim]^-$.



$[(TlMe_2)_2biim]$



$[TlMe_2(pyim)]$

Structures of the $(py)_2CH_2$, terpy, *and* Et_3terpy *Complexes.*— Aspects of the molecular geometry of the complexes are given in Tables 2—6, and views of the structures in the Figure.

The complexes have Tl–C 1.97(4)—2.139(13) Å, similar to reported values for crown ether complexes and $[TlMe_2(phen)]ClO_4$ containing neutral donor ligands [2.097(9)—2.180(17) Å],[1–4] and the nitrogen-donor ligands are chelated with Tl ··· N distances 2.61(3)—2.666(9) Å, within 3σ of the value for the phen complex, 2.57(3) Å.[1] The $(py)_2CH_2$ and Et_3terpy complexes have thallium ··· nitrate distances of 2.72(2)—3.11(3) Å, similar to the Tl ··· O distances in the crown ether [2.694(10)—2.979(5) Å][2–4] and perchlorate [2.88(3) Å][1] complexes. The terpy complex has a water molecule weakly interacting with thallium, 2.932(12) Å, and a nitrate ion at a distance 3.250(19) Å, corresponding to that expected for a van der Waals or weak electrostatic interaction, *ca.* 3.36 Å, using Pauling's radius for oxygen (1.4 Å)[17] and Bondi's estimated radius of 1.96 Å for thallium.[18] It is thus formulated as $[TlMe_2(terpy)(H_2O)]NO_3$.

Table 2. Specific crystallographic details

Complex	$[\{TlMe_2[(py)_2CH_2](NO_3)\}_2]$	$[TlMe_2(terpy)(H_2O)]NO_3$	$[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$
Formula	$(C_{13}H_{16}N_3O_3Tl)_2$	$C_{17}H_{19}N_4O_4Tl$	$C_{48}H_{64}N_9O_9Tl_3$
M	933.4	547.7	1 524.2
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/c$; no. 14	$P2_1/c$; no. 14	$I4_1/a$; no. 88
a/Å	8.923(3)	9.779(3)	15.715(6)
b/Å	22.535(8)	13.290(3)	
c/Å	7.527(3)	14.380(4)	45.21(1)
β/°	96.78(3)	93.95(2)	
U/Å^3	1 503(1)	1 864.5(8)	11 165(7)
D_c/g cm^{-3}	2.06	1.95	1.81
Z	2 dimers	4	8
F(000)	880	1 048	5 840
μ_{Mo}/cm^{-1}	104	84	84
Specimen/mm	0.33 × 0.32 × 0.24	0.28 × 0.43 × 0.18	0.25 × 0.40 × 0.34
Absorption factor (min., max.)	4.6, 12.2	4.3, 8.8	4.3, 8.5
$2\theta_{max.}$/°	60	60	40
N	4 416	5 462	2 619
N_o	2 739	3 000	1 547
R	0.048	0.061	0.071
R'	0.056	0.063	0.062

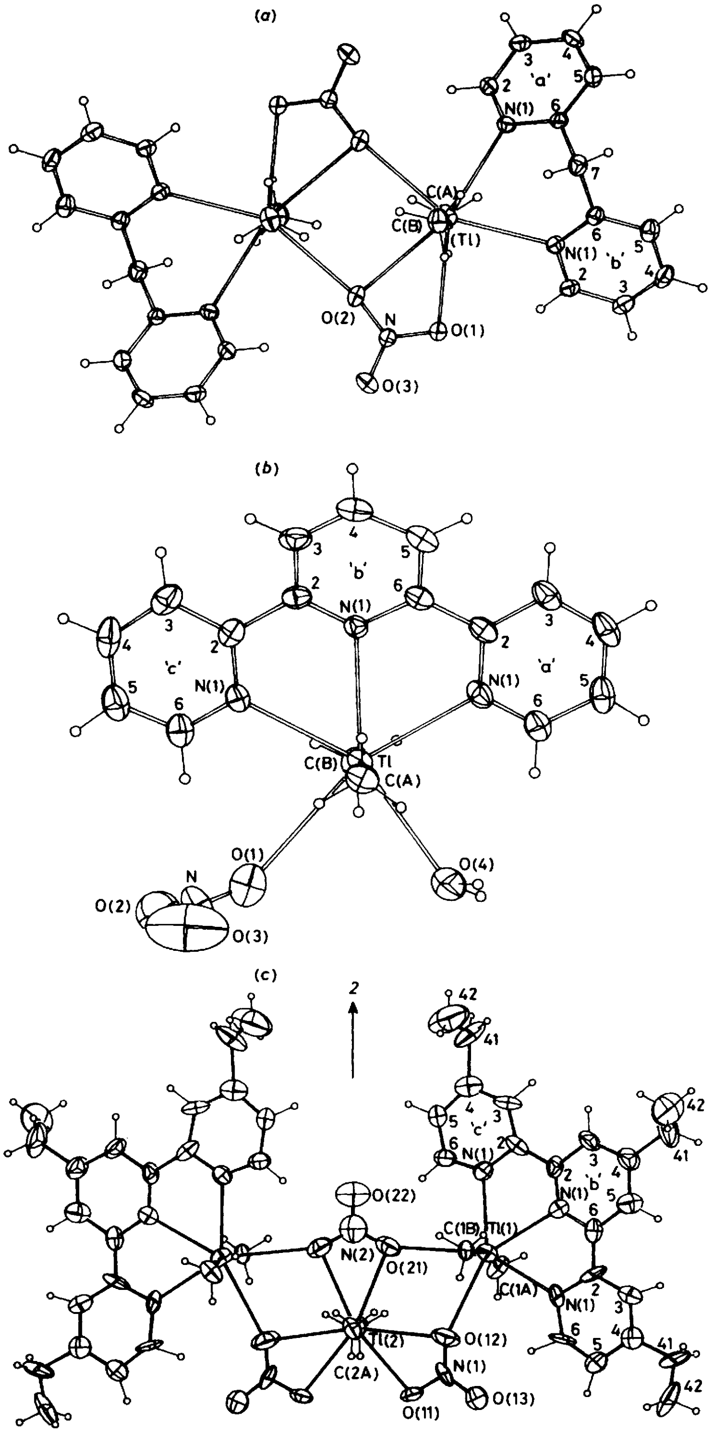


Figure. Structures of (*a*) [{$TlMe_2[(py)_2CH_2](NO_3)$}$_2$], (*b*) [$TlMe_2(terpy)(H_2O)$]NO_3, and (*c*) [$(TlMe_2)_3(Et_3terpy)_2(NO_3)_3$] projected normal to the equatorial 'planes' in each case; 20% thermal ellipsoids are shown for the non-hydrogen atoms together with atom numbering. Hydrogen atoms are shown with an arbitrary radius of 0.1 Å

The nitrate groups in the $(py)_2CH_2$ complex link two '$TlMe_2${$(py)_2CH_2$}' moieties to give a centrosymmetric dimer [{$TlMe_2[(py)_2CH_2](NO_3)$}$_2$] with a '$TlC_2N_2O_3$' co-ordination environment. For the Et_3terpy complex, two '$TlMe_2(Et_3$terpy)' moieties are weakly linked by a '$TlMe_2(NO_3)_3$' group to give an aggregate of stoicheiometry [$(TlMe_2)_3(Et_3terpy)_2(NO_3)_3$] having a two-fold axis and co-ordination environments '$TlC_2N_3O_2$' and 'TlC_2O_6.'

In all three complexes the $[TlMe_2]^+$ group is bent, with the C–Tl–C angle 166(1)—171.7(5)° opposite the Tl···N interactions, except for the 'TlC_2O_6' group in the Et_3terpy complex where a symmetrical 'TlO_6' donor set [Tl···O 2.72(2)—2.85(3) Å] results in a linear $[TlMe_2]^+$ group.

The pyridyl rings and nitrate groups are planar, with maximum deviations from the mean planes observed for C(2) of ring c in the Et_3terpy complex (−0.06 Å) and for O(2) of the

Table 3. Non-hydrogen atom co-ordinates for [{$TlMe_2[(py)_2CH_2](NO_3)$}$_2$]

Feature	Atom	*x*	*y*	*z*
$TlMe_2$				
	Tl	0.178 24(5)	0.058 09(2)	0.429 19(5)
	C(A)	0.045(2)	0.065 2(6)	0.174(2)
	C(B)	0.287(2)	0.041 4(6)	0.688(2)
$(py)_2CH_2$				
	N(a1)	0.165(1)	0.175 4(4)	0.471(1)
	C(a2)	0.030(1)	0.200 2(5)	0.422(2)
	C(a3)	0.008(1)	0.259 0(5)	0.389(2)
	C(a4)	0.132(2)	0.295 1(5)	0.405(2)
	C(a5)	0.272(2)	0.272 3(6)	0.450(2)
	C(a6)	0.286(1)	0.211 5(5)	0.480(1)
	C(7)	0.439(1)	0.181 6(6)	0.531(1)
	N(b1)	0.417(1)	0.104 7(4)	0.301(1)
	C(b2)	0.458(1)	0.079 4(5)	0.153(2)
	C(b3)	0.572(1)	0.100 7(6)	0.065(2)
	C(b4)	0.651(1)	0.148 8(7)	0.132(2)
	C(b5)	0.609(1)	0.175 8(6)	0.287(2)
	C(b6)	0.490(1)	0.152 6(5)	0.364(1)
Nitrate				
	N	0.205(1)	−0.082 1(5)	0.331(1)
	O(1)	0.301(1)	−0.044 8(4)	0.307(1)
	O(2)	0.099(1)	−0.067 4(4)	0.420(2)
	O(3)	0.217(1)	−0.133 2(4)	0.282(1)

Table 4. Non-hydrogen atom co-ordinates for $[TlMe_2(terpy)(H_2O)]NO_3$

Feature	Atom	*x*	*y*	*z*
$TlMe_2$				
	Tl	0.308 23(4)	0.202 30(4)	0.093 91(3)
	C(A)	0.258(2)	0.275(1)	0.219(1)
	C(B)	0.395(1)	0.137(1)	−0.023(1)
terpy				
	N(a1)	0.156(1)	0.324 0(8)	−0.012 6(7)
	C(a2)	0.019(1)	0.315(1)	−0.017 3(8)
	C(a3)	−0.061(1)	0.382(1)	−0.070 8(9)
	C(a4)	0.002(2)	0.457(1)	−0.118 9(9)
	C(a5)	0.141(2)	0.466(1)	−0.113 5(10)
	C(a6)	0.215(1)	0.397(1)	−0.059 2(9)
	N(b1)	0.045(1)	0.155 9(7)	0.065 2(6)
	C(b2)	−0.006(1)	0.080 1(10)	0.110 2(8)
	C(b3)	−0.142(1)	0.078(1)	0.130 2(9)
	C(b4)	−0.226(1)	0.152(1)	0.101 9(10)
	C(b5)	−0.177(1)	0.238(1)	0.052(1)
	C(b6)	−0.039(1)	0.235 0(9)	0.034 8(8)
	N(c1)	0.226(1)	0.022 6(7)	0.142 9(7)
	C(c2)	0.093(1)	−0.000 4(9)	0.140 9(8)
	C(c3)	0.050(2)	−0.095 3(11)	0.167 3(9)
	C(c4)	0.150(2)	−0.164 5(10)	0.197 2(10)
	C(c5)	0.283(2)	−0.140 2(11)	0.199 5(10)
	C(c6)	0.315(1)	−0.047 7(10)	0.171 7(10)
Nitrate				
	N	0.573(1)	0.091(1)	0.321(1)
	O(1)	0.542(2)	0.130(1)	0.252(1)
	O(2)	0.575(2)	0.118(3)	0.396(1)
	O(3)	0.626(2)	0.022(1)	0.305(1)
Water				
	O(4)	0.520(1)	0.355 7(9)	0.075 3(9)

Table 5. Non-hydrogen atom co-ordinates for $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$

Feature	Atom	*x*	*y*	*z*
$TlMe_2$ groups				
	Tl(1)	0.754 89(9)	0.152 19(9)	0.009 22(3)
	Tl(2)	1	1/4	−0.042 01(4)
	C(1A)	0.782(2)	0.029(3)	−0.001 1(7)
	C(1B)	0.747(2)	0.285(2)	0.011 2(7)
	C(2A)	1.040(2)	0.131(2)	−0.042 3(7)
Et_3terpy				
	N(a1)	0.614(2)	0.139(2)	−0.021 6(9)
	C(a2)	0.541(4)	0.124(2)	−0.006 9(10)
	C(a3)	0.465(3)	0.118(2)	−0.022 0(10)
	C(a4)	0.461(3)	0.123(2)	−0.051 9(13)
	C(a41)	0.373(4)	0.117(4)	−0.067 1(9)
	C(a42)	0.383(3)	0.131(4)	−0.095 1(15)
	C(a5)	0.535(3)	0.132(3)	−0.068 5(10)
	C(a6)	0.603(3)	0.138(3)	−0.051 9(9)
	N(b1)	0.612(2)	0.123(1)	0.039 0(8)
	C(b2)	0.619(3)	0.124(2)	0.068 6(12)
	C(b3)	0.547(3)	0.117(3)	0.086 4(9)
	C(b4)	0.467(3)	0.109(3)	0.073 2(12)
	C(b41)	0.392(4)	0.085(4)	0.093(2)
	C(b42)	0.370(4)	0.141(6)	0.108(2)
	C(b5)	0.465(3)	0.112(3)	0.042 0(12)
	C(b6)	0.540(3)	0.121(2)	0.023 5(13)
	N(c1)	0.768(2)	0.132(2)	0.066 4(6)
	C(c2)	0.698(3)	0.123(2)	0.084 0(10)
	C(c3)	0.718(4)	0.123(3)	0.114 0(10)
	C(c4)	0.799(4)	0.125(3)	0.125 8(11)
	C(c41)	0.801(6)	0.112(6)	0.162 0(18)
	C(c42)	0.829(9)	0.152(7)	0.172 9(20)
	C(c5)	0.864(3)	0.133(3)	0.105 3(13)
	C(c6)	0.850(3)	0.128(3)	0.075 9(10)
Nitrate groups				
	N(1)	0.833(2)	0.196(2)	−0.075(1)
	O(11)	0.900(2)	0.206(2)	−0.088 6(5)
	O(12)	0.827(2)	0.201(2)	−0.049 5(6)
	O(13)	0.771(2)	0.183(2)	−0.092 0(7)
	N(2)	1	1/4	0.027(2)
	O(21)	0.945(2)	0.203(2)	0.014 8(5)
	O(22)	1	1/4	0.052(1)

nitrate group in the terpy complex (0.06 Å). The thallium atoms lie close to the projected planes of the pyridyl rings (deviations of 0.00—0.27 Å), except for ring a of the $(py)_2CH_2$ complex (−0.74 Å) and ring b of the terpy complex (1.07 Å). The dihedral angles between the pyridyl rings of Et_3terpy are small, 3.1° for rings a, b and 2.5° for rings b, c, and are similar to those observed for other terpy complexes, *e.g.* 2.4 and 4.9° for $[Co(terpy)Cl_2]$.[19] However, consistent with the large deviation of Tl from the plane of ring b of the terpy complex, much larger dihedral angles are observed between the rings of terpy, 17.2 and 18.0°, similar to those observed for $[HgMe(Et_3terpy)]NO_3$ (15.4 and 18.6°) where the mercury atom also shows large deviations from the pyridyl mean planes (0.886, 0.121, and 1.032 Å).[5]

The weakly co-ordinating atoms in the equatorial region around $[TlMe_2]^+$ are approximately coplanar for the $(py)_2CH_2$ complex, where the atom deviations from the mean plane for 'TlN_2O_3' are +0.01 to −0.18 Å; similarly, for the 'TlN_3O_2'

Table 6. Thallium environments in the complexes. Entries in the first column, *r*, are the thallium–ligand distances (Å); other entries in the matrix are the angles (°) subtended at Tl by the relevant atoms at the head of the row and column

(*a*) $[\{TlMe_2[(py)_2CH_2](NO_3)\}_2]$

Atom	*r*	C(B)	N(a1)	N(b1)	O(1)	O(2)	O(2′)
C(A)	2.139(13)	171.7(5)	90.3(4)	91.7(4)	87.9(4)	86.7(4)	86.4(5)
C(B)	2.108(13)		95.1(4)	95.9(4)	90.0(4)	86.2(4)	88.3(4)
N(a1)	2.666(9)			72.5(3)	153.3(3)	162.0(3)	80.1(3)
N(b1)	2.658(9)				81.0(3)	125.3(3)	152.5(3)
O(1)	2.770(9)					44.3(3)	126.3(3)
O(2)	2.915(10)						82.0(3)
O(2′)	2.847(12)						

Deviations (Å) of atoms from the 'TlN_2O_3' mean plane: Tl, 0.01; N(a1), −0.06; N(b1), −0.07; O(1), −0.09; O(2), −0.04; O(2′), −0.18. For the nitrate group: N–O(1,2,3) are 1.23(1), 1.27(1), and 1.22(1) Å, with the angles opposite O(1,2,3) being 120(1), 121(1), and 119(1)°; Tl–O(1,2)–N, are 102.2(7) and 94.0(7)°; Tl–O(2)–Tl′ is 98.0(3) and N–O(2)–Tl′ 165.8(8)°. For the $(py)_2CH_2$ group: Tl–N(a1)–C(2,6) are 115.4(7) and 123.9(7)°; Tl–N(b1)–C(2,6) are 116.2(7) and 125.2(7)°; and Tl is 0.74 and 0.14 Å from the mean planes of rings a and b, respectively. The prime refers to atoms related through the centre of symmetry $(-x, -y, 1 - z)$.

(*b*) $[TlMe_2(terpy)(H_2O)]NO_3$

Atom	*r*	C(B)	O(4)	O(1)	N(a1)	N(b1)	N(c1)
C(A)	2.131(15)	169.6(6)	88.2(5)	74.5(5)	93.6(5)	87.7(5)	95.2(5)
C(B)	2.116(14)		83.6(5)	97.6(5)	91.9(4)	102.6(4)	89.1(5)
O(4)	2.932(12)			78.5(4)	83.9(3)	146.3(3)	152.3(3)
O(1)	3.250(19)				158.9(4)	131.9(4)	76.0(4)
N(a1)	2.620(10)					63.0(3)	123.1(3)
N(b1)	2.650(9)						61.3(3)
N(c1)	2.631(10)						

Deviations (Å) of atoms from the 'TlN_3O_2' mean plane: Tl, 0.00; N(a1) −0.07; N(b1), 0.23; N(c1), −0.21; O(1), 0.73; O(4), 0.00. For the nitrate group: N–O(1,2,3) are 1.15(3), 1.13(3), and 1.09(2) Å; with the angles opposite O(1,2,3) being 120(2), 107(2), and 132(2)°; Tl–O(1)–N is 151(1)°. For the terpy group: Tl–N(a1)–C(2,6) are 120.0(8) and 119.8(8)°; Tl–N(b1)–C(2,6) 120.1(7) and 114.8(7)°; Tl–N(c1)–C(2,6) 121.1(8) and 121.2(8)°; and Tl is 0.09, 1.07, and 0.03 Å from the mean planes of rings a, b, and c.

(*c*) $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$

Atom	*r*	C(1B)	O(12)	O(21)	N(a1)	N(b1)	N(c1)
(*i*) Tl(1)							
C(1A)	2.04(4)	166(1)	88(1)	94(1)	89(1)	97(1)	95(1)
C(1B)	2.09(4)		79(1)	78(1)	93(1)	96(1)	95(1)
O(12)	2.99(3)			70(1)	83(1)	145(1)	152(1)
O(21)	3.11(3)				151(1)	145(1)	83(1)
N(a1)	2.62(3)					63(1)	126(1)
N(b1)	2.66(3)						63(1)
N(c1)	2.61(3)						

Deviations (Å) of atoms from the 'TlN_3O_2' mean plane: Tl, 0.00; N(a1), −0.09; N(b1), 0.25; N(c1), 0.02; O(12), 0.10; O(21), 0.13. For the Et_3terpy group: Tl–N(a1)–C(2,6) are 118(3) and 129(3)°; Tl–N(b1)–C(2,6) 116(2) and 117(3)°; Tl–N(c1)–C(2,6) 121(3) and 113(3)°; and Tl is 0.00, 0.24, and 0.27 Å from the mean planes of rings a, b, and c.

(*ii*) Tl(2); primed atoms are generated by the two-fold rotor

Atom	*r*	O(11)	O(12)	O(21)
C(2A)	1.97(4)	87(1)	93(1)	82(1)
O(11)	2.72(2)		44(1)	118(1)
O(12)	2.85(3)			75(1)
O(21)	2.81(2)			

Deviations (Å) of atoms from the 'TlO_6' mean planes: Tl, 0.00; O(12,12′), 0.26, −0.26; O(11,11′), −0.08, 0.08; O(21,21′), −0.38, 0.38. For the nitrate groups: N(1)–O(11—13) are 1.22(5), 1.17(5), and 1.26(5) Å; N(2)–O(21,22) are 1.27(5) and 1.09(9) Å; with the angles O(11—13) at N(1) 123(4), 113(4), and 124(4)°, and the angles opposite O(21,22) at N(2) 117(4) and 127(4)°; Tl(2)–O(11,12)–N(1) are 98(2) and 93(3)°; Tl(1)–O(12)–N(1), Tl(2) are 154(3) and 109(1)°; Tl(2)–O(21)–N(2) is 93(4)°; and Tl(1)–O(21)–N(2), Tl(2) are 147(3) and 107(1)°.

group in the Et_3terpy complex, deviations of +0.25 to −0.09 Å occur (Table 6). The 'TlN_3O_2' mean plane of the terpy complex has atom deviations of +0.23 to −0.21 Å, except for the more distant nitrate oxygen, O(1)[Tl ··· O 3.25(2) Å, +0.73 Å from mean plane]. For the 'TlO_6' mean plane in the Et_3terpy complex, atoms O(12), O(11′), and O(21′) occur 0.26, 0.08, and 0.38 Å from the plane, with the corresponding atoms related by the two-fold axis on the opposite side of the plane, so that alternate oxygens occur above and below the plane.

The work reported here indicates that nitrogen-donor ligands bind to dimethylthallium(III) in methanol, and for the three complexes whose structures have been determined crystallographically the C–Tl–C groups are slightly bent away from the nitrogen-donor ligands which bind more strongly than the nitrate groups. Complex co-ordination geometries occur, involving weakly bridging nitrate groups in two complexes, with thallium geometries characterised by strong thallium–carbon bonding, and the presence of weak Tl···N and/or Tl···O interactions in approximate equatorial planes to give '$TlC_2N_2O_3$', '$TlC_2N_3O_2$,' and 'TlC_2O_6.'

Experimental

Dimethylthallium(III) iodide and nitrate,[20,21] 4,4′-diethyl-2,2′-bipyridyl (Et_2bipy),[22] *N*-methyl-2-(pyridin-2-yl)imidazole (pymim),[5] bis(pyridin-2-yl)methane [$(py)_2CH_2$],[23] bis(*N*-methylimidazol-2-yl)methanol [$(mim)_2CHOH$],[24] 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl (Et_3terpy),[25] and 2-(pyridin-2-yl)-imidazole[26] were prepared as described. The remaining ligands were obtained commercially, and were used as received. Proton spectra were measured at 300 MHz with a Bruker AM-300 instrument, i.r. spectra of complexes as Nujol and hexachlorobutadiene mulls between KBr plates with a Hitachi 270—30 spectrophotometer. Molecular weights were measured with a Knauer vapour-pressure osmometer. Microanalyses were by the Australian Microanalytical Service, Melbourne.

Syntheses.—Nitrate complexes. These complexes were obtained as colourless crystals in 28—37% yield. In a typical synthesis, dimethylthallium(III) nitrate (0.304 g, 1.03 mmol) was added to 4,4′-diethyl-2,2′-bipyridyl (0.193 g, 0.909 mmol) in acetone (30 cm^3) and the suspension stirred for 4 h. The suspension was filtered to remove a small quantity of undissolved dimethylthallium(III) nitrate, and the colourless filtrate allowed to evaporate slowly. At low volume, crystals of [$TlMe_2(Et_2bipy)$]NO_3 were collected, washed with cold acetone, and dried under vacuum over P_2O_5 (0.13 g, 28%).

[$TlMe_2L$] (L = pyim *or* pybzim). The silver(I) complexes Ag(pyim) and Ag(pybzim) were obtained using the method described for related complexes of silver(I),[27] involving addition of a solution of silver(I) nitrate in concentrated NH_3(aq) to solutions of py–Him and py–Hbzim in ethanol. The cream-coloured precipitates were collected, washed with ethanol, and dried under vacuum over P_2O_5. In a typical preparation, a mixture of dimethylthallium(III) iodide (0.867 g, 2.40 mmol) and Ag(pyim) (0.597 g, 2.37 mmol) in dry, distilled, dichloromethane (30 cm^3) was refluxed under nitrogen until yellow silver(I) iodide was observed, and then refluxed for 1 h. On cooling, AgI was removed by filtration through Celite under nitrogen, and the filtrate reduced to low volume by rotary evaporation. The remaining solvent was removed on a vacuum line, giving a pale pink solid, [$TlMe_2$(pyim)] (0.683 g, 76%). The complex [$TlMe_2$(pybzim)] is pale yellow.

[$(TlMe_2)_2L$] (L = biim *or* bibzim). In a typical synthesis, dimethylthallium(III) iodide (1.489 g, 4.12 mmol) was added to an almost boiling, filtered, solution obtained by addition of sodium hydroxide (*ca.* 1 g) to 2,2′-bi-imidazole (0.323 g, 2.41 mmol) in water (30 cm^3). The light brown precipitate formed was collected, washed with water, and dried under vacuum over P_2O_5. The crude complex was recrystallised by dissolution in acetone (30 cm^3), filtration to remove a small quantity of insoluble residue, and evaporation to low volume. Yellow-brown crystals of [$(TlMe_2)_2$biim] were collected, washed with cold acetone (*ca.* 1 cm^3), and dried under vacuum over P_2O_5 (1.014 g, 70%). Crude [$(TlMe_2)_2$bibzim] was recrystallised from chloroform, following a similar procedure (57%).

Crystallography.—Unique data sets were measured to the specified $2\theta_{max.}$ limit at 295 K using a Syntex $P\bar{1}$ four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source, and operating in conventional 2θ—θ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block-diagonal least-squares refinement after analytical absorption correction, and solution of the structure by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; estimated values of x,y,z, and U_{iso} for hydrogen atoms were included. Residuals R,R' (statistical weights) at convergence are quoted on $|F|$. Neutral complex scattering factors were used;[28] computation used the XTAL 83 program system[29] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Key results and atom numbering are given in the Figure and Tables 2—6.

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