The Preparation and Co-ordination Chemistry of 2,2′:6′,2″-Terpyridine Macrocycles. Part 4.[1] Structural Characterisation of an Intermediate in a Transient Template Reaction†

Edwin C. Constable, Fatima K. Khan, Jack Lewis,* Michael C. Liptrot, and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The complex $[SnMe_2L]Cl_2$ [L = 6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridine] is involved in the dimethyltin(IV) mediated transient template condensation of L with glyoxal; the complex has been structurally characterised, and shown to possess a pentagonal-bipyramidal geometry about the metal. The transient template effect is seen to originate in a reduction in the hole size of the N_5 donor set on passing from the open-chain ligand to the macrocycle.

We have recently described the template synthesis of quinquedentate N_5 donor macrocyclic complexes incorporating a 2,2′:6′,2″-terpyridine moiety in the ligand.[1-3] We have also described a novel 'transient' template effect in which hole-size mismatch effects result in the formation of metal-free macrocycles. In particular, we have demonstrated the use of dimethyltin(IV) as a transient template,[1] and in this paper we discuss the crystal and molecular structure of a macrocyclic precursor incorporating a dimethyltin(IV) group.

Experimental

Crystal and Molecular Structure Determination of $[SnMe_2L][PF_6]Cl$.—The reaction between dimethyltin(IV) dichloride and 6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridine (L) in refluxing chlorobenzene leads to the formation of $[SnMe_2L]Cl_2$ as a pale yellow salt. Recrystallisation from methanol in the presence of one mol equiv. of ammonium hexafluorophosphate yielded yellow rectangular crystals corresponding to $[SnMe_2L][PF_6]Cl$.

The crystals were air stable and several were mounted on glass fibres: a crystal of dimensions *ca.* 0.426 × 0.334 × 0.293 mm was used for data collection.

Crystal data. $[C_{25}H_{29}N_7Sn][PF_6]Cl$, $M = 726.66$, triclinic, $a = 7.899(3)$, $b = 11.104(3)$, $c = 17.276(4)$ Å, $\alpha = 98.66(2)$, $\beta = 95.13(3)$, $\gamma = 107.08(2)^\circ$, $U = 1\,417.55$ Å^3 (by least-squares refinement from 40 automatically centred reflections in the range $15 < 2\theta < 25^\circ$), space group $P\bar{1}$ (no. 2), D_m not measured, $Z = 2$, $D_c = 1.702$ g cm^{-3}, $F(000) = 728$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 10.79$ cm^{-1}.

Data collection and processing.[4] A Stoe four-circle diffractometer, in ω/θ scan mode with a minimum ω scan width of 1.2°, scan speed 0.0125—0.05° s^{-1}, was used with graphite-monochromated Mo-K_α radiation; 5 384 reflections were measured ($5.0 < 2\theta < 50.0^\circ$, $+h$, $\pm k$, $\pm l$). 4 276 Unique observed reflections [$F > 4\sigma(F)$] were obtained after averaging and correcting for absorption (transmission factors, 0.191—0.237).

Structure analysis and refinement. The Sn atom was located by a Patterson synthesis, and remaining non-hydrogen atoms from subsequent Fourier difference syntheses. Blocked-cascade least-squares refinement with all non-hydrogen atoms assigned anisotropic thermal parameters. Methyl and aromatic ring H atoms were placed in geometrically idealised positions. Methyl groups were treated as rigid bodies, and each type of H assigned a common isotropic thermal parameter. The hydrazine H atoms were not located. The weighting scheme $w = 1/[\sigma^2(F) + 0.0005|F|^2]$ gave satisfactory agreement analyses. Final R and R' values are 0.062 and 0.067. All computations were performed on the University of Cambridge IBM 370/165 computer using a version of SHELX.[5] Complex neutral-atom scattering factors were employed.[6] The final atomic fractional co-ordinates are listed in Table 1.

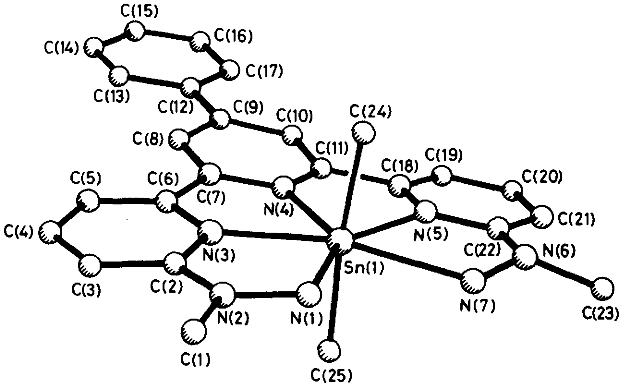

Figure. Molecular structure of the $[SnMe_2L]^{2+}$ cation

Results and Discussion

Description of the Structure.—The molecular structure of the $[SnMe_2L]^{2+}$ cation is illustrated in the Figure, along with the numbering scheme adopted. The hydrogen atoms have been omitted for clarity. Associated bond lengths and bond angles are given in Tables 2 and 3 respectively.

X-Ray analysis confirms the presence of a slightly distorted pentagonal-bipyramidal N_5C_2 tin(IV) environment. The N_5 donor set of atoms defining the equatorial plane are coplanar (the maximum deviation from the least-squares plane is 0.03 Å) and the tin atom is coplanar with this plane. The two axial positions are taken up by two co-ordinated methyl groups.

The angles subtended by adjacent nitrogen-donor atoms at the tin(IV) centre lie in the range 68—82°. The largest angle of 81.9(2)° for N(1)–Sn(1)–N(7) is in keeping with the non-bonded distance of 3.22(1) Å between atoms N(1) and N(7). The Sn(1)–N(1)–N(2) and Sn(1)–N(7)–N(6) angles suggest sp^3 hybridization at N(1) and N(7), although this cannot be unequivocally established since the amine hydrogen atoms were not located directly. The two non-co-ordinated nitrogen atoms, N(2) and N(6), display planar sp^2 hybridization with the sum of the bond angles around them being 356.4 and 360.0° respectively.

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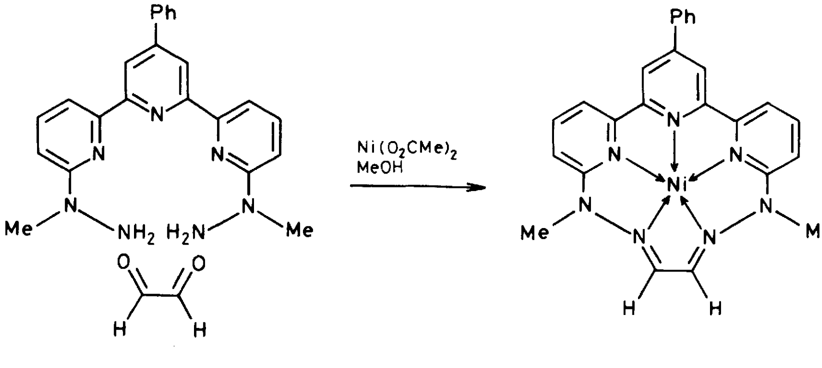
† *Supplementary data available* (No. SUP 56103, 5 pp.): H-atom co-ordinates, thermal parameters, hydrogen-bond angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates (× 10^4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn(1)	10 965(1)	2 529(1)	3 151(1)
N(1)	13 671(11)	4 353(7)	3 431(4)
N(2)	14 211(10)	4 816(7)	2 732(4)
C(1)	15 759(15)	5 926(10)	2 846(6)
N(3)	11 822(8)	3 130(5)	1 995(3)
C(2)	13 223(10)	4 196(7)	2 015(4)
C(3)	13 680(11)	4 642(7)	1 312(5)
C(4)	12 626(11)	3 950(8)	602(4)
C(5)	11 208(10)	2 849(7)	584(4)
C(6)	10 858(9)	2 475(6)	1 289(4)
N(4)	9 041(8)	1 210(5)	2 100(3)
C(7)	9 339(9)	1 353(7)	1 346(4)
C(8)	8 277(10)	504(7)	699(4)
C(9)	6 810(9)	−534(6)	789(4)
C(10)	6 500(10)	−624(7)	1 566(4)
C(11)	7 636(9)	242(6)	2 199(4)
C(12)	5 620(9)	−1 410(6)	113(4)
C(13)	5 861(11)	−1 259(7)	−678(4)
C(14)	4 739(11)	−2 109(8)	−1 305(4)
C(15)	3 308(11)	−3 130(8)	−1 188(5)
C(16)	3 039(11)	−3 286(7)	−445(5)
C(17)	4 179(10)	−2 432(7)	213(4)
N(5)	8 724(8)	1 000(5)	3 579(3)
C(18)	7 426(10)	179(7)	3 047(4)
C(19)	5 934(11)	−692(7)	3 254(4)
C(20)	5 892(12)	−709(8)	4 055(5)
C(21)	7 257(11)	121(8)	4 608(4)
C(22)	8 647(10)	999(7)	4 361(4)
N(6)	10 043(9)	1 824(7)	4 884(3)
C(23)	9 933(13)	2 030(10)	5 747(4)
N(7)	11 337(11)	2 823(7)	4 619(4)
C(24)	12 616(12)	1 325(8)	3 169(5)
C(25)	9 482(15)	3 842(8)	3 278(5)
P(1)	9 704(3)	2 688(2)	8 217(1)
F(1)	9 477(9)	3 628(6)	8 985(4)
F(2)	11 771(8)	3 016(7)	8 602(4)
F(3)	10 064(13)	1 802(6)	7 500(4)
F(4)	9 214(11)	1 522(6)	8 685(4)
F(5)	10 265(10)	3 855(6)	7 781(4)
F(6)	7 707(9)	2 386(9)	7 872(5)
Cl(1)	3 640(2)	−3 596(2)	5 066(1)

Table 2. Bond lengths (Å)

Sn(1)–N(1)	2.425(7)	C(11)–C(18)	1.499(10)	Sn(1)–N(3)	2.295(6)	C(12)–C(13)	1.425(10)
Sn(1)–N(4)	2.268(5)	C(12)–C(17)	1.396(10)	Sn(1)–N(5)	2.326(6)	C(13)–C(14)	1.372(9)
Sn(1)–N(7)	2.489(6)	C(14)–C(15)	1.400(11)	Sn(1)–C(24)	2.126(10)	C(15)–C(16)	1.349(12)
Sn(1)–C(25)	2.121(12)	C(16)–C(17)	1.411(9)	N(1)–N(2)	1.435(10)	N(5)–C(18)	1.325(8)
N(2)–C(1)	1.432(11)	N(5)–C(22)	1.358(9)	N(2)–C(2)	1.368(9)	C(18)–C(19)	1.401(10)
N(3)–C(2)	1.356(8)	C(19)–C(20)	1.390(11)	N(3)–C(6)	1.356(8)	C(20)–C(21)	1.375(10)
C(2)–C(3)	1.415(11)	C(21)–C(22)	1.385(11)	C(3)–C(4)	1.395(10)	C(22)–N(6)	1.361(9)
C(4)–C(5)	1.388(10)	N(6)–C(23)	1.488(10)	C(5)–C(6)	1.371(10)	N(6)–N(7)	1.434(10)
C(6)–C(7)	1.477(9)	P(1)–F(1)	1.618(7)	N(4)–C(7)	1.368(9)	P(1)–F(2)	1.620(7)
N(4)–C(11)	1.344(8)	P(1)–F(3)	1.563(8)	C(7)–C(8)	1.376(8)	P(1)–F(4)	1.600(7)
C(8)–C(9)	1.413(9)	P(1)–F(5)	1.568(7)	C(9)–C(10)	1.399(10)	P(1)–F(6)	1.555(8)
C(9)–C(12)	1.456(8)			C(10)–C(11)	1.388(8)		



Scheme.

The two outer pyridine rings make angles of 8.0 and 7.0° with the central pyridine ring, and the dihedral angle between this central ring and the phenyl ring is 2.4°. This suggests that while a completely planar system would give maximum π-overlap a slight twisting of the ring system reduces steric crowding between the ring hydrogens. Even with this distortion there are a number of intramolecular ring-hydrogen contacts which are significantly shorter than the sum of the van der Waals radii of 2.4 Å: H(5) ··· H(8), 2.026; H(8) ··· H(13), 1.925; H(10) ··· H(17), 1.877; H(10) ··· H(19), 2.030 Å.

The chloride and the hexafluorophosphate anions are not co-ordinated to the cation.

The Sn–N bond distances fall in the range 2.27—2.49 Å; the long Sn–N(amine) [2.425(7) and 2.489(6) Å] and the shorter Sn–N(terminal pyridine) [2.295(6) and 2.326(6) Å] and Sn–N(central pyridine) [2.268(5) Å] bonds are similar to the Sn–N bond distances found in the cation of the compound [$SnMe_2Cl$(terpy)][$SnMe_2Cl_3$], the adduct formed from the reaction of dimethyltin(IV) dichloride and 2,2′:6′,2″-terpyridine (terpy).[7] An analogy is also found in the pentagonal-

Table 3. Bond angles (°)

N(1)–Sn(1)–N(3)	69.8(2)	Sn(1)–N(5)–C(22)	121.3(4)	C(2)–C(3)–C(4)	117.5(6)
N(1)–Sn(1)–N(5)	150.5(2)	C(11)–C(18)–N(5)	115.8(6)	C(4)–C(5)–C(6)	117.8(6)
N(1)–Sn(1)–C(24)	87.9(3)	N(5)–C(18)–C(19)	122.8(6)	N(3)–C(6)–C(7)	114.3(6)
N(3)–Sn(1)–N(4)	69.9(2)	C(19)–C(20)–C(21)	120.3(7)	Sn(1)–N(4)–C(7)	120.3(4)
N(3)–Sn(1)–N(7)	151.7(2)	N(5)–C(22)–C(21)	120.7(6)	C(7)–N(4)–C(11)	118.5(5)
N(3)–Sn(1)–C(25)	91.5(3)	C(21)–C(22)–N(6)	121.6(7)	C(6)–C(7)–C(8)	123.5(6)
N(4)–Sn(1)–N(7)	138.3(2)	C(22)–N(6)–N(7)	119.8(6)	C(7)–C(8)–C(9)	121.0(6)
N(4)–Sn(1)–C(25)	93.8(3)	Sn(1)–N(7)–N(6)	111.6(4)	C(8)–C(9)–C(12)	122.0(6)
N(5)–Sn(1)–C(24)	89.8(3)	F(1)–P(1)–F(3)	175.9(5)	C(9)–C(10)–C(11)	120.6(6)
N(7)–Sn(1)–C(24)	87.5(3)	F(1)–P(1)–F(5)	90.0(4)	N(4)–C(11)–C(18)	114.1(5)
C(24)–Sn(1)–C(25)	172.8(3)	F(2)–P(1)–F(3)	88.8(5)	C(9)–C(12)–C(13)	121.7(6)
N(1)–N(2)–C(1)	116.3(7)	F(2)–P(1)–F(5)	89.5(4)	C(13)–C(12)–C(17)	117.0(6)
C(1)–N(2)–C(2)	124.8(8)	F(3)–P(1)–F(4)	90.6(4)	C(13)–C(14)–C(15)	121.2(7)
Sn(1)–N(3)–C(6)	120.3(4)	F(3)–P(1)–F(6)	92.8(5)	C(15)–C(16)–C(17)	120.7(7)
N(2)–C(2)–N(3)	118.2(7)	F(4)–P(1)–F(6)	91.3(5)	Sn(1)–N(5)–C(18)	118.8(5)
N(3)–C(2)–C(3)	121.0(6)	N(1)–Sn(1)–N(4)	139.7(2)	C(18)–N(5)–C(22)	119.6(6)
C(3)–C(4)–C(5)	121.3(7)	N(1)–Sn(1)–N(7)	81.9(2)	C(11)–C(18)–C(19)	121.3(5)
N(3)–C(6)–C(5)	123.1(6)	N(1)–Sn(1)–C(25)	88.1(3)	C(18)–C(19)–C(20)	117.1(6)
C(5)–C(6)–C(7)	122.6(5)	N(3)–Sn(1)–N(5)	139.7(2)	C(20)–C(21)–C(22)	119.4(7)
Sn(1)–N(4)–C(11)	121.2(4)	N(3)–Sn(1)–C(24)	92.8(3)	N(5)–C(22)–N(6)	117.6(6)
C(6)–C(7)–N(4)	115.0(5)	N(4)–Sn(1)–N(5)	69.8(2)	C(22)–N(6)–C(23)	120.7(7)
N(4)–C(7)–C(8)	121.4(6)	N(4)–Sn(1)–C(24)	93.1(3)	C(23)–N(6)–N(7)	115.9(6)
C(8)–C(9)–C(10)	116.1(5)	N(5)–Sn(1)–N(7)	68.6(2)	F(1)–P(1)–F(2)	87.2(4)
C(10)–C(9)–C(12)	121.8(6)	N(5)–Sn(1)–C(25)	90.7(3)	F(1)–P(1)–F(4)	89.2(4)
N(4)–C(11)–C(10)	122.3(6)	N(7)–Sn(1)–C(25)	86.0(3)	F(1)–P(1)–F(6)	91.2(4)
C(10)–C(11)–C(18)	123.6(6)	Sn(1)–N(1)–N(2)	112.5(4)	F(2)–P(1)–F(4)	88.1(4)
C(9)–C(12)–C(17)	121.3(6)	N(1)–N(2)–C(2)	118.9(6)	F(2)–P(1)–F(6)	178.3(4)
C(12)–C(13)–C(14)	120.6(7)	Sn(1)–N(3)–C(2)	120.2(4)	F(3)–P(1)–F(5)	90.0(4)
C(14)–C(15)–C(16)	119.4(6)	C(2)–N(3)–C(6)	119.4(6)	F(4)–P(1)–F(5)	177.5(4)
C(12)–C(17)–C(16)	121.1(7)	N(2)–C(2)–C(3)	120.7(6)	F(5)–P(1)–F(6)	91.1(5)

bipyramidal complex $[SnMe_2(terpy)(NCS)_2]$, which has bond lengths Sn–N(terminal pyridine) of 2.479(3) and 2.570(4) Å, and Sn–N(central pyridine) of 2.497(3) Å.[8]

The condensation of L with glyoxal to produce the Schiff-base macrocycle L′ (Scheme) proceeds readily about a nickel(II) or manganese (II) template; in each case the product is the metal complex of the macrocycle L′.[1] In the absence of a template ion, predominantly polymeric products are obtained. When dimethyltin(IV) is used as the template ion, the metal-free macrocycle L′ is obtained. The labilisation of the tin(IV) in the macrocyclic complex is undoubtedly thermodynamic in origin (the formation of SnO_2), although we consider the reduction of hole size from the hydrazine (2.32 Å) to the macrocycle (2.10 Å) results in destabilisation of the macrocyclic complex.

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