

also hydrogen bonded to the five water molecules with F...O contacts in the range 2.60 (1)–3.07 (2) Å. The water molecules of crystallization are both hydrogen bonded among themselves and to N and F atoms of the cation and anion respectively. A more detailed analysis of the hydrogen-bond scheme is hampered by the fact that H atoms for the water molecules could not be identified owing to their high thermal motion. In addition to the observed dynamic disorder of the water molecules there are also indications for some static disorder. The presence of relatively strong hydrogen bridges was also inferred from the infrared spectrum of this compound, where strong bands in the 2500–3200 cm⁻¹ region occurred.

The bond angles around the thioether S atoms are close to 100°, which indicates that one of the lone electron pairs on each of these sulfurs is directed towards the Ni. The relatively long Ni–S(8) and Ni–S(9) contacts of 2.513 (2) and 2.496 (2) Å respectively suggest weak bonds, but are rather normal for Ni–S(thioether) distances (Setzer, Ogle, Wilson & Glass, 1983; Hill & Hope, 1974). The imidazole rings are planar within 0.008 Å.

The geometry of the SiF₆ anion is the same as reported for [Cu(H₂O)₆]₂SiF₆ (Ray, Zalkin & Templeton, 1973).

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1-(2,2':6',2''-Terpyridine)-2-methyl-3-trimethylsilyl-2,3-dicarba-1-stanna-closo-heptaborane(6)–2,2':6',2''-Terpyridine

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Abstract. C₂₁H₂₇B₄N₃SiSn.C₁₅H₁₁N₃, *M_r* = 744.82, triclinic, *P*1̄, *a* = 8.304 (1), *b* = 13.161 (2), *c* = 17.493 (3) Å, *α* = 105.74 (1), *β* = 91.96 (1), *γ* = 92.84 (1)°, *V* = 1835.5 (5) Å³, *Z* = 2, *D_x* = 1.35 g cm⁻³, *λ*(Mo *Kα*) = 0.71069 Å, *μ* = 7.61 cm⁻¹, *F*(000) = 760, *T* = 295 K. Final *R* = 0.040 for 5550 observed reflections. The Lewis base 2,2':6',2''-terpyridine forms a donor–acceptor complex (II) with closo-1-Sn-2-(Me)-3-(SiMe₃)-2,3-C₂B₄H₄ (I). This complex (II) has a distorted pentagonal bipyramidal geometry

with the Sn atom occupying an apical position. Specifically, the complex shows extreme displacement of the tin from the centroidal position above the C₂B₃ face of the carborane cage. The Sn–C(cage) bond distances are about 0.43 Å longer than the Sn–B(unique) distance which is definitely shorter than the other two Sn–B distances by about 0.168 Å. The slippage is such that the Sn^{II} atom could be considered as η¹-bonded to the unique B of the carborane cage. The apical Sn is also bonded strongly to two consecutive N atoms and weakly to the third N atom of the terpyridine rings on the opposite side of the C₂B₃ ring.

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In addition, a terpyridine molecule is solvated with each donor-acceptor complex of the stannacarborane in the unit cell and these are not within the van der Waals distances. One of the interesting features of the structure is the overall nonplanarity of the coordinated terpyridine with respect to each of the pyridine rings in the uncoordinated terpyridine molecule. Bond distances in the cage structure are Sn—C = 2.828 (3), Sn—B = 2.570 (4), 2.396 (4), and 2.559 (4), Sn—N = 2.687 (3), 2.573 (3) and 2.560 (3) Å; the B—Sn—N bond angles are 74.3 (1) to 133.5 (1)°.

Introduction. Our work in the area of *closo* main-group heterocarboranes of the type 1-*M*-2-(SiMe₃)-3-(*R*)-2,3-C₂B₄H₄ (*M* = Ge, Sn; *R* = SiMe₃, Me or H) and their donor-acceptor complexes with Lewis bases has raised several fundamental questions regarding the bonding of the heteroatom to the carborane cage (Hosmane & Maguire, 1987; Cowley, Galow, Hosmane, Jutzi & Norman, 1984; Hosmane, de Meester, Maldar, Potts, Chu & Herber, 1986; Siriwardane, Hosmane & Chu, 1987; Hosmane, Islam, Siriwardane, Maguire & Campana, 1987; Hosmane, Siriwardane, Islam, Maguire & Chu, 1987). The distinctive dislocation of the heteroatom away from the C₂B₃ centroid axis that exists in all the donor-acceptor complexes of the stanna- and germacarboranes as well as the slight slippage of the tin in the stannacarboranes seems to be independent of the oxidation state of the heteroatom and whether or not the metal has filled or empty *d* orbitals. Such slippage has been observed in a number of 'capped' and 'sandwiched' transition-metal and main-group-metal carborane complexes and a number of explanations for this distortion have been proposed. Since many of the arguments used to account for distortions in transition-metal complexes invoke *d* orbitals and/or electrons (Colquhoun, Greenough & Wallbridge, 1985; Mingos, 1977; Mingos, Forsyth & Welch, 1978), they are not directly applicable to the Group 14 metal-lacarboranes. Several qualitative arguments have been made on the slippage of the heteroatom from the centroidal position, that is, away from the cage carbons and toward the three boron atoms of the C₂B₃ ring (Calhorda, Mingos & Welch, 1982; Canadell, Eisenstein & Rubio, 1984). The recent molecular-orbital calculations of the Fenske-Hall type on the 'experimental' geometries of the (2,2'-bipy)SnB₄H₄(CCH₃)₂ (Barreto, Fehlner & Hosmane, 1988) and MNDO-SCF calculations on *closo*-Sn(R₂C₂B₄H₄) (Maguire, Ford & Hosmane, 1988) support these qualitative arguments. The only structural information available to date in the small carborane system is that for the *closo*-1-Sn-[2-(SiMe₃)-3-(*R*)-2,3-C₂B₄H₄] (*R* = SiMe₃, Me, H), and the donor-acceptor complexes *closo*-1-Sn-(2,2'-C₁₀H₈N₂)-2-(SiMe₃)-3-(*R*)-2,3-C₂B₄H₄ (*R* = SiMe₃ and Me), 1,1'-(2,2'-C₈H₆N₂)-[*closo*-1-Sn-2,3-(SiMe₃)₂-2,3-C₂B₄H₄]₂ and *closo*-1-Ge-(2,2'-C₁₀H₈N₂)-2,3-(SiMe₃)₂-

2,3-C₂B₄H₄ (Hosmane & Maguire, 1987). Indeed, very little is known regarding the Lewis-acid behavior of these heterocarboranes. In all the donor-acceptor complexes, only two donor N atoms are involved in bonding with the two *p* orbitals of the metal atom that were originally involved in π bonding with the filled carborane orbitals. To date, it is not known whether the apical heteroatom in the heterocarboranes would bond to three or more donor atoms of the Lewis base that would result in any drastic changes in the bonding of the metal to the C₂B₃ face of the carborane fragment. During the course of our investigation in this area, we sought to examine the reactivity of the *closo*-stannacarborane toward a tridentate Lewis base and its structural consequences upon complexation, if the complexation could be accomplished at all. Upon stirring a benzene solution of *closo*-1-Sn-2-(Me)-3-(SiMe₃)-2,3-C₂B₄H₄ (I) with 2,2':6',2''-terpyridine (C₁₅H₁₁N₃) in a millimolar ratio of 1:2 at 273 K, a reddish-brown solid formed slowly, indicating that a complexation had occurred between the reactants. This reaction produced in high yield a previously unknown stannacarborane complex (II), which was isolated as a moderately air-stable reddish-brown crystalline and sublimable solid. Since the complex (II) is sparingly soluble in most of the organic solvents, its structure could not be determined by spectroscopy. Therefore, an X-ray analysis of the crystalline solid (II) was undertaken that unambiguously confirmed the solid to be the new stannacarborane-terpyridine complex, *closo*-1-Sn(2,2':6',2''-C₁₅H₁₁N₃)-2-(Me)-3-(SiMe₃)-2,3-C₂B₄H₄ (II), as represented in its ORTEP drawing (Johnson, 1965) of Fig. 1.

Experimental. The title compound (II) was isolated in 85% yield as a reddish-brown solid in a reaction involving stannacarborane and terpyridine in benzene at 273 K. Large well formed rhombohedral crystals of (II) were grown by sublimation of the reddish-brown

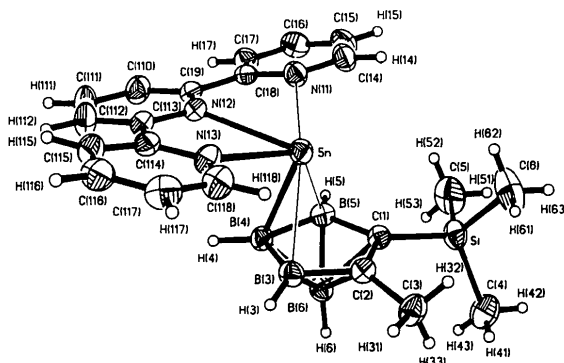


Fig. 1. ORTEP (Johnson, 1965) drawing of (II) without the solvate 2,2':6',2''-terpyridine. Thermal ellipsoids scaled to enclose 35% probability. H atoms are represented as spheres of arbitrary radii. The weaker bonding interactions are shown by thinner lines.

solid in a sealed Pyrex glass tube. A single crystal (0.37 × 0.35 × 0.25 mm) was coated with an epoxy resin; unit-cell parameters by least-squares fit of 25 reflections in the range 10 ≤ 2θ ≤ 25°; space group *P* $\bar{1}$, automatic Nicolet R3m/V diffractometer, graphite-monochromated MoK α radiation, $\theta/2\theta$ scan mode (scan rate 3.0–14.0° min⁻¹, depending upon the intensity), 6816 measured reflections, 6571 unique reflections in the range 3 ≤ 2θ ≤ 55°, $R_{\text{int}} = 0.014$; *hkl* range *h*–8–8, *k*–14–14, *l*0→18; 5550 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics; three standard reflections remeasured after every 100 reflections did not show any significant change in intensity during the data collection; Lorentz–polarization correction, no absorption or extinction corrections. Structure solved by direct methods (Sheldrick, 1986, *SHELXTL-Plus*) and subsequent difference Fourier methods. H atoms were directly located on difference Fourier maps except for silyl-methyl hydrogens. All hydrogens were included with isotropic temperature factors; methyl, silyl-methyl and aromatic ring hydrogens were geometrically constrained. Final full-matrix least-squares refinement (Sheldrick, 1986) converged to $R = 0.040$ and $wR = 0.043$; $S = 1.39$ for 483 parameters, $(\Delta/\sigma)_{\text{max}} = 0.015$, $\Delta\rho_{(\text{max}, \text{min})} = 0.41, -0.29 \text{ e \AA}^{-3}$ in the final difference Fourier map, $w = 1/(\sigma^2 F + 0.000349 F^2)$, $\sum w(|F_o| - |F_c|)^2$ minimized. Atomic scattering factors for C, H, N, B, Si, Sn and real and imaginary parts of the dispersion corrections for Sn and Si were those stored in *SHELXTL-Plus*.

Discussion. The final atomic parameters of the non-H atoms are given in Table 1. The identification of the atoms and the configuration of (II) and the solvated 2,2':6',2''-terpyridine are shown in the *ORTEP* (Johnson, 1965) drawings of Figs. 1 and 2. The title compound (II) has a distorted pentagonal bipyramidal geometry with the Sn atom occupying an apical position and bonding strongly to two consecutive N atoms and weakly to the third N atom of the terpyridine rings on the opposite side of the C₂B₃ ring. In addition, a terpyridine molecule is solvated with each donor–acceptor complex of the stannacarborane in the unit cell, and these are not within the van der Waals distances (Fig. 3). The bond lengths and selected bond angles with their standard deviations are given in Table 2.* The distortion of the cage geometry is primarily due to Sn–C distances [2.832 (3) and 2.825 (4) Å] which are substantially longer than the Sn–B distances of

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Sn	4359 (1)	6262 (1)	8502 (1)	40 (1)
Si	4254 (2)	7377 (2)	6362 (1)	51 (1)
C(1)	3317 (7)	7094 (4)	7248 (3)	39 (2)
C(2)	2178 (7)	6187 (4)	7209 (3)	38 (2)
B(3)	1404 (9)	6238 (6)	8006 (4)	45 (3)
B(4)	2149 (8)	7391 (6)	8634 (4)	40 (2)
B(5)	3466 (9)	7879 (6)	8090 (4)	42 (2)
N(11)	6622 (6)	7820 (4)	9145 (3)	48 (2)
N(12)	4484 (6)	7100 (4)	10015 (3)	38 (2)
N(13)	2998 (6)	5172 (4)	9336 (3)	47 (2)
B(6)	1534 (9)	7399 (6)	7676 (4)	41 (2)
C(3)	1602 (8)	5400 (5)	6415 (3)	51 (3)
C(14)	7705 (7)	8112 (5)	8669 (4)	47 (4)
C(15)	8469 (7)	9119 (5)	8865 (4)	52 (4)
C(16)	8107 (8)	9836 (5)	9560 (4)	51 (4)
C(17)	6982 (7)	9522 (5)	10058 (4)	46 (4)
C(18)	6284 (7)	8498 (5)	9823 (3)	38 (2)
C(19)	5141 (7)	8090 (5)	10317 (3)	41 (2)
C(110)	4796 (8)	8698 (5)	11066 (4)	51 (3)
C(111)	3767 (9)	8277 (6)	11530 (4)	60 (4)
C(112)	3137 (8)	7250 (6)	11232 (4)	53 (5)
C(113)	3511 (7)	6675 (5)	10466 (4)	46 (2)
C(114)	2843 (7)	5577 (5)	10118 (4)	44 (2)
C(115)	2055 (8)	4994 (5)	10580 (4)	45 (4)
C(116)	1389 (8)	3966 (6)	10198 (4)	56 (4)
C(117)	1526 (8)	3567 (5)	9388 (4)	56 (4)
C(118)	2372 (8)	4187 (5)	8973 (4)	55 (4)
C(4)	2695 (9)	7544 (7)	5599 (4)	81 (5)
C(5)	5557 (8)	8641 (5)	6680 (4)	62 (8)
C(6)	5616 (10)	6292 (6)	5910 (5)	95 (6)
N(21)	6041 (8)	–1064 (5)	4277 (4)	78 (3)
N(22)	3141 (6)	–2001 (4)	3479 (3)	39 (2)
N(23)	1007 (8)	–571 (5)	3196 (4)	73 (3)
C(24)	7509 (8)	–637 (5)	4687 (4)	57 (4)
C(25)	8650 (8)	–1330 (6)	4812 (4)	60 (4)
C(26)	8305 (9)	–2410 (6)	4514 (4)	56 (5)
C(27)	6889 (7)	–2821 (4)	4127 (3)	47 (2)
C(28)	5783 (7)	–2167 (5)	4010 (4)	41 (2)
C(29)	4253 (7)	–2653 (5)	3599 (3)	41 (2)
C(210)	3963 (8)	–3759 (5)	3356 (4)	47 (3)
C(211)	2458 (8)	–4180 (5)	3011 (4)	53 (3)
C(212)	1294 (7)	–3504 (5)	2896 (3)	41 (4)
C(213)	1711 (8)	–2413 (5)	3132 (3)	42 (2)
C(214)	568 (8)	–1640 (5)	2978 (3)	42 (2)
C(215)	–853 (7)	–2059 (5)	2599 (4)	58 (2)
C(216)	–1885 (10)	–1382 (7)	2429 (5)	75 (5)
C(217)	–1551 (9)	–300 (6)	2612 (5)	62 (5)
C(218)	–61 (9)	125 (5)	3009 (4)	57 (4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.570 (4), 2.396 (4) and 2.559 (4) Å. However, these distances are somewhat different from those determined for (2,2'-C₁₀H₈N₂)Sn-(Me₃Si)(Me)C₂B₄H₄] (Siriwardane, Hosmane & Chu, 1987). Specifically, the Sn–B_(unique) distance in the title compound is significantly shorter (by 0.163–0.174 Å) than the other two Sn–B distances. The 'slip distortion' in (II) is such that the apical Sn atom could be considered as η^1 -bonded to the C₂B₃ face of the carborane fragment. One of the interesting features of the structure is the overall non-planarity of the coordinated 2,2':6',2''-terpyridine molecule with respect to each of the pyridine rings in the uncoordinated terpyridine molecule in the unit cell. It appears that there are no published crystallographic data on 2,2':6',2''-terpyridine itself. However, the crystal and molecular structure of 4'-phenyl-2,2':6',2''-terpyridine and the complex [Ni-(4'-phterpy)₂][PF₆]₂·10H₂O have been determined. In this study, the structure of the free ligand, 4'-phterpy, exhibits slight differences in bond lengths from the

* Lists of structure factors, anisotropic temperature factors, selected torsion angles, selected least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51033 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coordinated ligand, but the major differences arise from distortion of the terminal C₅N rings (Constable, 1986). The dihedral angles between the planes formed by the C₂B₃ face of the carborane cage and the C₅N rings of the terpyridine molecule containing N(11), N(12) and N(13) donor atoms in (II) are 14.0 (2), 10.0 (2) and 12.4 (2)°, respectively. Similar average angles in the other donor-acceptor complexes (2,2'-bipyrimidine)-[Sn(SiMe₃)₂C₂B₄H₄]₂, (2,2'-bipyridine)Sn(SiMe₃)₂C₂B₄H₄ and (2,2'-bipyridine)Sn(SiMe₃)(Me)C₂B₄H₄ are 44.21 (3), 26.8 (5) and 18.4 (2)°, respectively (Hosmane, Islam, Siriwardane, Maguire & Campana, 1987; Hosmane, de Meester, Maldar, Potts, Chu & Herber, 1986; Siriwardane, Hosmane & Chu, 1987). However, the dihedral angles between the pyridine rings in the coordinated terpyridine and the free terpyridine are 6.0 (2), 19.1 (2) and 13.1 (2)° and 5.0 (3), 6.6 (2) and 5.6 (2)°, respectively. It is clear that the complexed terpyridine is more distorted than the free terpyridine within the same unit cell. It is interesting to point out that the dihedral angle between the terminal and central C₅N rings within the coordinated terpyridine in [Ni(4'-phterpy)]₂[PF₆]₂·10H₂O increases from 5.7 to 7.1°, which is presumably due to increased ring strain in the complex (Constable, 1986). The Sn-N distances, [2.687 (3), 2.573 (3) and 2.560 (3) Å] in the title compound (II) are slightly longer than those in (CH₃)₂Sn(NCS)₂(2,2':6',2''-C₁₅H₁₁N₃) [2.479 (3), 2.497 (3) and 2.570 (4) Å] (Naik & Scheidt, 1973) and *closo*-(2,2'-C₁₀H₈N₂)Sn(Me₃Si)(R)C₂B₄H₄ [2.49 (1) and 2.54 (1) Å when R = SiMe₃; 2.474 (4) and

Table 2. Bond lengths (Å) and bond angles (°)

Sn-C(1)	2.832 (3)	Sn-C(2)	2.825 (4)
Sn-B(3)	2.570 (4)	Sn-B(4)	2.396 (4)
Sn-B(5)	2.559 (4)	Sn-N(11)	2.687 (3)
Sn-N(12)	2.573 (3)	Sn-N(13)	2.560 (3)
Si-C(1)	1.875 (4)	Si-C(4)	1.890 (5)
Si-C(5)	1.878 (4)	Si-C(6)	1.884 (4)
C(1)-C(2)	1.471 (5)	C(1)-B(5)	1.549 (6)
C(1)-B(6)	1.698 (5)	C(2)-B(3)	1.540 (6)
C(2)-B(6)	1.704 (5)	C(2)-C(3)	1.535 (5)
B(3)-B(4)	1.688 (6)	B(3)-B(6)	1.773 (6)
B(4)-B(5)	1.688 (6)	B(4)-B(6)	1.738 (6)
B(5)-B(6)	1.751 (6)	N(11)-C(14)	1.356 (5)
N(11)-C(18)	1.326 (4)	N(12)-C(19)	1.345 (5)
N(12)-C(113)	1.352 (5)	N(13)-C(114)	1.340 (5)
N(13)-C(118)	1.349 (5)	C(14)-C(15)	1.389 (5)
C(15)-C(16)	1.374 (5)	C(16)-C(17)	1.420 (5)
C(17)-C(18)	1.388 (5)	C(18)-C(19)	1.481 (5)
C(110)-C(111)	1.392 (5)	C(111)-C(112)	1.380 (6)
C(112)-C(113)	1.402 (5)	C(113)-C(114)	1.478 (5)
C(114)-C(115)	1.411 (5)	C(115)-C(116)	1.412 (6)
C(116)-C(117)	1.381 (6)	C(117)-C(118)	1.410 (5)
N(21)-C(24)	1.403 (5)	N(21)-C(28)	1.402 (5)
N(22)-C(29)	1.340 (5)	N(22)-C(213)	1.335 (5)
N(23)-C(214)	1.382 (5)	N(23)-C(218)	1.398 (5)
C(24)-C(25)	1.399 (6)	C(25)-C(26)	1.387 (6)
C(26)-C(27)	1.348 (5)	C(27)-C(28)	1.337 (5)
C(28)-C(29)	1.466 (5)	C(29)-C(210)	1.407 (5)
C(210)-C(211)	1.390 (5)	C(211)-C(212)	1.391 (5)
C(212)-C(213)	1.404 (5)	C(213)-C(214)	1.494 (5)
C(214)-C(215)	1.349 (5)	C(215)-C(216)	1.348 (6)
C(216)-C(217)	1.383 (7)	C(217)-C(218)	1.410 (6)
C(2)-Sn-C(1)	30.1 (1)	B(3)-Sn-C(1)	55.2 (1)
B(3)-Sn-C(2)	32.7 (1)	B(4)-Sn-C(1)	58.4 (1)
B(4)-Sn-C(2)	58.2 (1)	B(4)-Sn-B(3)	39.6 (1)
B(5)-Sn-C(1)	32.9 (1)	B(5)-Sn-C(2)	55.1 (1)
B(5)-Sn-B(3)	62.4 (1)	B(5)-Sn-B(4)	39.7 (1)
N(11)-Sn-C(1)	96.0 (1)	N(11)-Sn-C(2)	125.9 (1)
N(11)-Sn-B(3)	133.5 (1)	N(11)-Sn-B(4)	95.5 (1)
N(11)-Sn-B(5)	74.3 (1)	N(12)-Sn-C(1)	130.1 (1)
N(12)-Sn-C(2)	136.4 (1)	N(12)-Sn-B(3)	107.1 (1)
N(12)-Sn-B(4)	78.9 (1)	N(12)-Sn-B(5)	97.4 (1)
N(12)-Sn-N(11)	61.1 (1)	N(13)-Sn-C(1)	134.9 (1)
N(13)-Sn-C(2)	106.7 (1)	N(13)-Sn-B(3)	80.0 (1)
N(13)-Sn-B(4)	91.5 (1)	N(13)-Sn-B(5)	131.2 (1)
N(13)-Sn-N(11)	121.5 (1)	N(13)-Sn-N(12)	63.6 (1)
C(4)-Si-C(1)	112.5 (2)	C(5)-Si-C(1)	109.9 (2)
C(5)-Si-C(4)	107.0 (2)	C(6)-Si-C(1)	109.3 (2)
C(6)-Si-C(4)	111.1 (2)	C(6)-Si-C(5)	106.9 (2)
Si-C(1)-Sn	135.7 (2)	C(2)-C(1)-Sn	74.7 (2)
C(2)-C(1)-Si	124.3 (3)	B(5)-C(1)-Sn	63.8 (2)
B(5)-C(1)-Si	123.2 (3)	B(5)-C(1)-C(2)	111.9 (3)
B(6)-C(1)-Sn	91.2 (2)	B(6)-C(1)-Si	132.6 (3)
B(6)-C(1)-C(2)	64.6 (2)	B(6)-C(1)-B(5)	65.1 (3)
C(1)-C(2)-Sn	75.2 (2)	B(3)-C(2)-Sn	64.5 (2)
B(3)-C(2)-C(1)	113.2 (3)	B(6)-C(2)-Sn	91.3 (2)
B(6)-C(2)-C(1)	64.2 (2)	B(6)-C(2)-B(3)	66.0 (3)
C(3)-C(2)-Sn	137.9 (2)	C(3)-C(2)-C(1)	121.9 (3)
C(3)-C(2)-B(3)	123.9 (3)	C(3)-C(2)-B(6)	130.6 (3)
C(2)-B(3)-Sn	82.8 (2)	B(4)-B(3)-Sn	64.7 (2)
B(4)-B(3)-C(2)	105.3 (3)	B(6)-B(3)-Sn	98.6 (2)
B(6)-B(3)-C(2)	61.4 (2)	B(6)-B(3)-B(4)	60.2 (3)
B(3)-B(4)-Sn	75.8 (2)	B(5)-B(4)-Sn	75.4 (2)
B(5)-B(4)-B(3)	103.8 (3)	B(6)-B(4)-Sn	106.6 (2)
B(6)-B(4)-B(3)	62.3 (3)	B(6)-B(4)-B(5)	61.5 (2)
C(1)-B(5)-Sn	83.3 (2)	B(4)-B(5)-Sn	65.0 (2)
B(4)-B(5)-C(1)	105.6 (3)	B(6)-B(5)-Sn	99.6 (2)
B(6)-B(5)-C(1)	61.6 (2)	B(6)-B(5)-B(4)	60.7 (2)
C(14)-N(11)-Sn	119.2 (2)	C(18)-N(11)-Sn	116.4 (2)
C(18)-N(11)-C(14)	119.9 (3)	C(19)-N(12)-Sn	119.6 (2)
C(113)-N(12)-Sn	118.7 (2)	C(113)-N(12)-C(19)	119.1 (3)
C(114)-N(13)-Sn	121.2 (2)	C(118)-N(13)-Sn	119.1 (2)
C(118)-N(13)-C(114)	119.6 (3)	C(2)-B(6)-C(1)	51.2 (2)
B(3)-B(6)-C(1)	92.8 (3)	B(3)-B(6)-C(2)	52.5 (2)
B(4)-B(6)-C(1)	97.3 (3)	B(4)-B(6)-C(2)	96.4 (3)
B(4)-B(6)-B(3)	57.5 (2)	B(5)-B(6)-C(1)	53.3 (2)
B(5)-B(6)-C(2)	92.8 (3)	B(5)-B(6)-B(3)	97.8 (3)
B(5)-B(6)-B(4)	57.9 (2)	C(28)-N(21)-C(24)	118.5 (4)
C(213)-N(22)-C(29)	119.0 (3)	C(218)-N(23)-C(214)	118.9 (4)

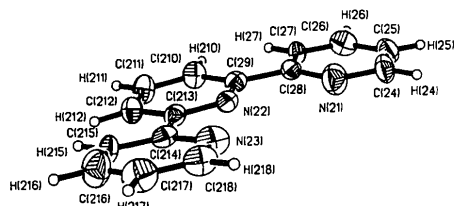


Fig. 2. ORTEP (Johnson, 1965) drawing of solvated 2,2':6',2''-terpyridine molecule. Thermal ellipsoids scaled to enclose 35% probability. H atoms are represented as spheres of arbitrary radii.

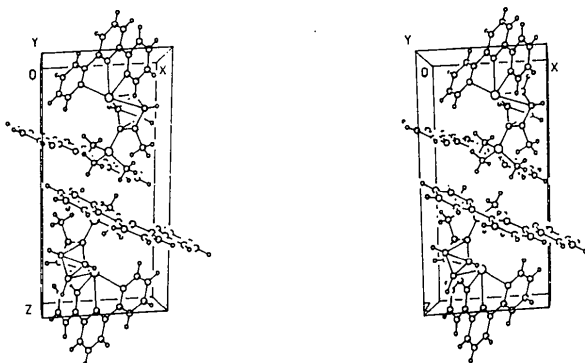


Fig. 3. Stereoscopic drawing of the molecular packing in the unit cell.

2.476 (4) Å when R = Me] (Hosmane, de Meester, Maldar, Potts, Chu & Herber, 1986; Siriwardane, Hosmane & Chu, 1987), but are comparable with those of the bridged donor-acceptor complex 1,1'-

(2,2'-C₈H₆N₄)-[*closo*-1-Sn-2,3-(Me₃Si)₂-2,3-C₂B₄H₄]₂ [2.639 (5) Å] (Hosmane, Islam, Siriwardane, Maguire & Campana, 1987). The B_(unique)-Sn-N bond angles are 95.5 (1), 78.9 (1) and 91.5 (2)°, thus indicating that the Lewis base is not symmetrically bonded to the apical Sn. One of the C₃N planes of the coordinated terpyridine molecule, in particular, the pyridine ring containing N(13), is significantly tilted [13.9 (2)°] from the overall plane of the terpyridine in (II). The mean and the highest deviations of the atoms of the complexed terpyridine from the calculated planes are 0.116 (5) and 0.315 (5) Å, respectively, and are significantly higher than those in the free terpyridine [0.051 (8) and 0.087 (8) Å]. Evidently, the C(115), C(116), N(13) and C(118) atoms of a pyridine ring are responsible for the highest deviation in the Lewis base by their respective values of 0.343 (6), 0.302 (6), -0.233 (4) and -0.252 (6) Å.

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Structure of a Peptide Surrogate, *tert*-Butoxycarbonylalanyl-ψ(CH₂S)-phenylalanine [Boc-Ala-ψ(CH₂S)-Phe-OH]

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Abstract. C₁₇H₂₅NO₄S, *M_r* = 339.5, monoclinic, *C*2, *a* = 24.927 (8), *b* = 5.252 (4), *c* = 16.867 (7) Å, β = 122.70 (1)°, *V* = 1858.2 (9) Å³, *Z* = 4, *D_x* = 1.21 g cm⁻³, λ(Mo Kα) = 0.71069 Å, μ = 1.83 cm⁻¹, *F*(000) = 728, *T* = 295 K. The final *R* value for 1466 independent observed reflections is 0.075. The thio-methylene dipeptide analogue possesses a C_{*i*}^α...C_{*i*+1}^α distance somewhat smaller than in the extended amide

counterpart due to a partially folded structure, especially in the C-terminal region. Pairs of molecules are held together by O-H...O=C (carboxylic acid) hydrogen bonds.

Introduction. Replacement or modification of peptide backbone functions with D-amino acids, N and α-C substituents, and unnatural amide-bond replacements