The commensurately modulated bis(aquachlorotriphenyltin·1, 10-phenanthroline) crystal structure

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Abstract Bis(aquachlorotriphenyltin.1,10-phenanthroline) [$P2_1/n$, $a = 21.1053(5)$, $b = 12.2347(3)$, $c = 51.772(2)$ Å, $\beta = 101.525(2)°$; $Z = 10$] has a diffraction pattern dominated by a set of strong reflections with $2h + l = 5N$. Average intensities for reflections with $2h + l = 5N$, $5N \pm 1$ and $5N \pm 2$ are in the ratio $1.000 : 0.157 : 0.075$, the differences between categories being more pronounced at lower θ angles. The structure is a commensurate displacive modulation of an idealized parent structure of $P2_1/c$ symmetry whose unit cell is one-fifth the volume of the $P2_1/n$ cell, the cell axes being given by $a_o = (2a + c)/5$, $b_o = -b$, $c_o = (3a - c)/5$ [i.e., $a_o = 11.9814(3)$, $b_o = 12.2347(3)$, $c_o = 17.8875(4)$ Å; $\beta = 92.418(2)°$]. The choice of a global phase for the modulation waves was an essential part of the structure determination as it distinguished between pseudo homometric structure solutions. The structure was refined to $R = 0.039$ for 3666 reflections.

Keywords Bis(aquachlorotriphenyltin.1,10-phenanthroline) – commensurately modulated – crystal structure

INTRODUCTION

The nature of the hydrogen-bonding interactions in the hydrated complex of triphenyltin chloride with 1,10-phenanthroline, which is the first example of a triorganotin entity that binds indirectly, through the coordinated water molecule, to the potentially bidentate 1,10-phenanthroline heterocycle, is of interest to the understanding of how triorganotin cations bind to nucleic acids. The dimeric complex (Scheme 1) was described in the monoclinic $P2_1/c$ space group [$a = 11.9602(7)$, $b = 12.2196(7)$, $c = 17.854(1)$ Å; $\beta = 92.409(6)°$]; the crystal structure could only be refined to $R = 0.128$, the large discrepancies between observed and calculated structure factors being attributed to "twinning" [1]. The isolation of this complex has led to studies on the 1,10-phenanthroline complexes of other triaryltin halides [2,3] and carboxylates [4-6] as well as on the triphenyltin complexes with other bidentate *N*-heterocycles [7-10]. The differing types of hydrogen bonds found in these 'outer-sphere coordination' complexes prompted a re-investigation of the parent complex, but we could not find the $P2_1/c$ cell although we were able to find a $P2_1/n$ cell that was five times as large and whose *b*-axis was identical to that of the reported cell. This observation was reproduced using crystals prepared in separate syntheses and using different diffractometers. *SHELXS*-97 [11] gave an initial solution for this 13,000 Å³ cell, but the refinement of the model with *SHELXL*-97 [11] required an excessive number of constraints and was later found to be incorrect as to its choice of global phase. We have refined the modulated structure by using the constrained refinement program *RAELS*00 [12], and we discuss here the implications of its commensurate nature.

EXPERIMENTAL

Synthesis and measurements

The colorless complex was obtained by reacting equimolar quantities of triphenyltin chloride and 1,10-phenanthroline. The reagents were heated in ethanol until they dissolved completely. Slow cooling of the filtered solution afforded large colorless crystals. The crystals are stable in air for several years. The room-temperature diffraction measurements on a cubic specimen were performed on a Nonius KappaCCD area-detector diffractometer ($\lambda = 0.71073$ Å) in the 2.01 to 27.50° θ-range. The 326,049 intensities were corrected for absorption effects [13]. The raw intensities were reduced by *DENZO-SCALEPACK* [14] for solution by *SHELXS*-97 [11]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 168882. *Crystal data*: $C_{60}H_{50}Cl_2N_4O_2Sn_2$, monoclinic, $P2_1/n$, $a = 21.1053(5)$, $b = 12.2347(3)$, $c = 51.772(2)$ Å, $\beta = 101.525(2)°$; $Z = 10$.

Refinements

The program *RAELS*00 that was used for refinement allows the use of refinable local coordinates relative to refinable orthonormal axial systems and the use of refinable *TLS* rigid-body thermal-motion parameters [15]. The 1,10-phenanthroline molecules and the C_6H_5 groups attached to Sn were constrained to have identical local planar geometry of *mm*2 symmetry. The Sn-O distances were all constrained to be equal. The axial systems of the C_6H_5 groups were restrained to approach coplanarity with the Sn atoms; the Sn-C-C angles were constrained to be equal. The Sn, Cl and O atoms were given individual atom anisotropic temperature parameters. The 1,10-phenanthroline molecules and C_6H_5 groups were each refined using separate 15-parameter *TLX* models, and 12-parameter *TL* models centered on the appropriate Sn atom, respectively. This permitted 524 degrees of freedom to describe meaningfully the 175 non-H atoms in the asymmetric unit from the refinement of 12317 reflections [out of 29,670 independent reflections obeying the $I > 3\sigma(I)$ cutoff] to obtain the final statistics (Table 1). H-atoms other than the water-H atoms were recalculated in sensible geometric positions after each refinement cycle and given thermal parameters determined by rigid parameters describing the atoms to which they were attached. There were no degrees of freedom advantages

Table 1. Statistics for the refinements on F for the commensurate structure of $[(C_6H_5)_3SnCl\cdot H_2O\cdot C_{12}H_8N_2]_2$.

Class*	No. of reflns.	$R(F)$	$R(F^2)$	wR	Gof**
$m = 0$	3666	0.039	0.057	0.063	1.48
$m = \pm 1$	4785	0.068	0.098	0.091	1.75
$m = \pm 2$	3866	0.078	0.119	0.089	1.53
All m	12317	0.057	0.068	0.081	1.60
Others	17353	0.458	0.626	0.500	1.60

* The reflections that were calculated but not included in refinement had $I < 3\sigma(I)$.

** Weighting scheme $w = [\text{var}(|F_{obs}|) + (0.03\,|F_{obs}|)^2]^{-1}$.

Table 2. Atomic coordinates and equivalent isotropic temperature factors for $[(C_6H_5)_3SnCl\cdot H_2O\cdot C_{12}H_8N_2]_2$.*

Atom	X	y	z	U_{eq}
Sn1a	0.69461(2)	0.55834(4)	0.51650(1)	0.0516(1)
Cl1a	0.8148(1)	0.5757(2)	0.5232(1)	0.064(1)
O1a	0.5813(1)	0.5112(2)	0.5061(1)	0.072(1)
C21a	0.6872(1)	0.5623(2)	0.4753(1)	0.053(2)
C22a	0.6634(2)	0.6534(3)	0.4608(1)	0.077(3)
C23a	0.6589(3)	0.6566(4)	0.4336(1)	0.090(3)
C24a	0.6780(2)	0.5687(4)	0.4208(1)	0.089(3)
C25a	0.7016(3)	0.4776(4)	0.4348(1)	0.123(4)
C26a	0.7062(3)	0.4745(3)	0.4619(1)	0.100(3)
C31a	0.7008(1)	0.4190(3)	0.5411(1)	0.052(2)
C32a	0.7350(2)	0.3273(3)	0.5364(1)	0.068(2)
C33a	0.7390(2)	0.2361(3)	0.5526(1)	0.086(3)
C34a	0.7089(2)	0.2357(4)	0.5737(1)	0.085(3)
C35a	0.6748(2)	0.3255(4)	0.5788(1)	0.080(3)
C36a	0.6708(2)	0.4167(3)	0.5625(1)	0.065(2)
C41a	0.6760(1)	0.7083(3)	0.5346(1)	0.058(3)
C42a	0.7238(2)	0.7863(3)	0.5414(1)	0.069(2)
C43a	0.7118(3)	0.8839(3)	0.5532(1)	0.087(2)
C44a	0.6518(3)	0.9045(4)	0.5584(1)	0.104(4)
C45a	0.6038(2)	0.8285(4)	0.5518(1)	0.118(4)
C46a	0.6158(2)	0.7310(4)	0.5400(1)	0.089(2)
N1a	0.4941(1)	0.5082(3)	0.5510(1)	0.061(1)
C2a	0.4834(2)	0.6004(3)	0.5629(1)	0.080(2)
C3a	0.4781(2)	0.6044(4)	0.5897(1)	0.095(2)
C4a	0.4843(2)	0.5098(4)	0.6037(1)	0.087(2)
C5a	0.5024(2)	0.3105(4)	0.6058(1)	0.076(2)
C6a	0.5131(2)	0.2179(3)	0.5939(1)	0.075(2)
C7a	0.5294(2)	0.1214(3)	0.5539(1)	0.084(2)
C8a	0.5339(2)	0.1242(4)	0.5280(1)	0.094(2)
C9a	0.5269(2)	0.2257(4)	0.5148(1)	0.082(2)
N10a	0.5162(1)	0.3182(3)	0.5266(1)	0.062(2)
C11a	0.5002(1)	0.4143(3)	0.5651(1)	0.053(1)
C12a	0.5118(1)	0.3149(3)	0.5523(1)	0.053(2)
C13a	0.4955(1)	0.4123(4)	0.5919(1)	0.065(1)
C14a	0.5183(1)	0.2163(3)	0.5668(1)	0.064(1)
Sn1b	0.30137(2)	0.57217(4)	0.31400(1)	0.0493(1)
Cl1b	0.4213(1)	0.5921(2)	0.3203(1)	0.067(1)
O1b	0.1866(1)	0.5373(2)	0.3030(1)	0.059(1)
C21b	0.2877(1)	0.5702(2)	0.2725(1)	0.059(3)
C22b	0.2724(3)	0.6645(3)	0.2579(1)	0.110(3)
C23b	0.2635(3)	0.6634(4)	0.2305(1)	0.135(4)
C24b	0.2698(2)	0.5680(5)	0.2175(1)	0.099(4)
C25b	0.2848(3)	0.4736(4)	0.2316(1)	0.101(3)
C26b	0.2937(2)	0.4747(3)	0.2589(1)	0.087(3)
C31b	0.3076(1)	0.4312(3)	0.3381(1)	0.051(2)
C32b	0.2709(2)	0.3393(3)	0.3300(1)	0.066(2)
C33b	0.2753(2)	0.2469(3)	0.3458(1)	0.075(3)
C34b	0.3164(2)	0.2454(4)	0.3699(1)	0.092(3)
C35b	0.3532(3)	0.3354(4)	0.3783(1)	0.139(4)
C36b	0.3488(2)	0.4278(3)	0.3624(1)	0.108(4)
C41b	0.2849(1)	0.7241(2)	0.3319(1)	0.053(3)
C42b	0.3327(2)	0.7728(3)	0.3505(1)	0.064(2)
C43b	0.3220(2)	0.8712(3)	0.3623(1)	0.081(3)
C44b	0.2633(2)	0.9219(3)	0.3556(1)	0.087(4)
C45b	0.2152(2)	0.8753(3)	0.3373(1)	0.084(3)
C46b	0.2260(2)	0.7769(3)	0.3255(1)	0.066(2)
N1b	0.1211(1)	0.5194(3)	0.3455(1)	0.057(1)
C2b	0.1334(2)	0.6171(3)	0.3566(1)	0.074(1)
C3b	0.1576(2)	0.6310(4)	0.3838(1)	0.089(1)
C4b	0.1687(2)	0.5407(4)	0.3994(1)	0.085(1)
C5b	0.1672(2)	0.3401(4)	0.4039(1)	0.082(2)

	x	y	z	U_{eq}
C6b	0.1549(2)	0.2421(3)	0.3929(1)	0.084(2)
C7b	0.1171(2)	0.1295(3)	0.3533(1)	0.088(2)
C8b	0.0939(2)	0.1227(3)	0.3269(1)	0.087(2)
C9b	0.0837(2)	0.2204(4)	0.3121(1)	0.068(2)
N10b	0.0959(1)	0.3182(3)	0.3230(1)	0.054(1)
C11b	0.1322(1)	0.4298(3)	0.3611(1)	0.055(1)
C12b	0.1190(1)	0.3245(3)	0.3493(1)	0.055(1)
C13b	0.1564(1)	0.4378(4)	0.3885(1)	0.069(1)
C14b	0.1304(1)	0.2303(3)	0.3653(1)	0.071(2)
Sn1c	0.88819(2)	0.57183(4)	0.10905(1)	0.0470(1)
Cl1c	1.0077(1)	0.5938(2)	0.1131(1)	0.064(1)
O1c	0.7734(1)	0.5381(2)	0.1026(1)	0.056(1)
C21c	0.8672(1)	0.5723(2)	0.0671(1)	0.050(2)
C22c	0.8512(2)	0.6679(3)	0.0531(1)	0.076(2)
C23c	0.8374(3)	0.6684(4)	0.0257(1)	0.092(3)
C24c	0.8395(2)	0.5732(4)	0.0121(1)	0.080(2)
C25c	0.8552(3)	0.4776(4)	0.0255(1)	0.086(2)
C26c	0.8690(2)	0.4772(3)	0.0529(1)	0.072(2)
C31c	0.8970(1)	0.4293(2)	0.1330(1)	0.050(2)
C32c	0.8569(2)	0.3401(3)	0.1262(1)	0.054(2)
C33c	0.8628(2)	0.2474(3)	0.1419(1)	0.062(2)
C34c	0.9087(2)	0.2428(3)	0.1646(1)	0.082(3)
C35c	0.9489(2)	0.3299(4)	0.1717(1)	0.109(3)
C36c	0.9431(2)	0.4227(3)	0.1560(1)	0.085(2)
C41c	0.8735(1)	0.7218(2)	0.1282(1)	0.051(2)
C42c	0.9223(2)	0.7681(3)	0.1468(1)	0.067(2)
C43c	0.9128(2)	0.8652(3)	0.1593(1)	0.081(3)
C44c	0.8543(2)	0.9171(3)	0.1534(1)	0.080(2)
C45c	0.8053(2)	0.8729(3)	0.1351(1)	0.082(3)
C46c	0.8149(2)	0.7758(3)	0.1226(1)	0.067(2)
N1c	0.7154(1)	0.5147(3)	0.1477(1)	0.056(1)
C2c	0.7278(2)	0.6128(3)	0.1585(1)	0.078(1)
C3c	0.7512(2)	0.6279(4)	0.1858(1)	0.101(2)
C4c	0.7614(2)	0.5383(5)	0.2016(1)	0.099(2)
C5c	0.7589(2)	0.3381(4)	0.2067(1)	0.093(2)
C6c	0.7465(2)	0.2396(4)	0.1960(1)	0.093(2)
C7c	0.7096(2)	0.1254(3)	0.1566(1)	0.095(3)
C8c	0.6871(2)	0.1174(3)	0.1301(1)	0.097(2)
C9c	0.6778(2)	0.2143(4)	0.1151(1)	0.074(2)
N10c	0.6900(1)	0.3126(3)	0.1257(1)	0.054(2)
C11c	0.7257(1)	0.4258(3)	0.1636(1)	0.055(1)
C12c	0.7124(1)	0.3201(3)	0.1521(1)	0.054(1)
C13c	0.7490(1)	0.4350(4)	0.1910(1)	0.076(1)
C14c	0.7228(1)	0.2266(3)	0.1683(1)	0.074(2)
Sn1d	0.50030(2)	0.56795(4)	0.91038(1)	0.0469(1)
Cl1d	0.6184(1)	0.5778(2)	0.9099(1)	0.064(1)
O1d	0.3864(1)	0.5368(2)	0.9081(1)	0.060(1)
C21d	0.4705(1)	0.5711(2)	0.8688(1)	0.052(3)
C22d	0.4683(2)	0.6680(3)	0.8549(1)	0.091(3)
C23d	0.4486(3)	0.6705(4)	0.8277(1)	0.112(4)
C24d	0.4307(2)	0.5761(4)	0.8140(1)	0.088(4)
C25d	0.4325(3)	0.4793(4)	0.8273(1)	0.091(3)
C26d	0.4523(2)	0.4768(3)	0.8545(1)	0.076(3)
C31d	0.5123(1)	0.4287(3)	0.9352(1)	0.047(2)
C32d	0.5336(2)	0.3305(3)	0.9269(1)	0.071(2)
C33d	0.5419(2)	0.2394(3)	0.9432(1)	0.086(3)
C34d	0.5288(2)	0.2457(3)	0.9680(1)	0.071(3)
C35d	0.5076(2)	0.3420(4)	0.9767(1)	0.067(2)
C36d	0.4994(2)	0.4330(3)	0.9603(1)	0.058(2)
C41d	0.4955(1)	0.7197(3)	0.9306(1)	0.049(2)
C42d	0.5392(2)	0.8027(3)	0.9293(1)	0.060(2)
C43d	0.5362(2)	0.9010(3)	0.9424(1)	0.076(2)
C44d	0.4895(2)	0.9174(3)	0.9569(1)	0.081(3)
C45d	0.4457(2)	0.8365(4)	0.9584(1)	0.077(3)
C46d	0.4487(2)	0.7381(3)	0.9453(1)	0.061(2)
N1d	0.3064(1)	0.5256(3)	0.9485(1)	0.077(2)
C2d	0.2959(2)	0.6275(4)	0.9553(1)	0.119(2)
C3d	0.3044(2)	0.6610(4)	0.9819(1)	0.174(2)
C4d	0.3241(2)	0.5857(5)	1.0012(1)	0.178(2)
C5d	0.3562(2)	0.3965(5)	1.0141(1)	0.182(4)
C6d	0.3668(2)	0.2943(5)	1.0073(1)	0.185(5)
C7d	0.3684(2)	0.1571(4)	0.9725(1)	0.191(5)
C8d	0.3592(2)	0.1311(4)	0.9464(1)	0.187(4)
C9d	0.3387(2)	0.2140(4)	0.9277(1)	0.127(2)
N10d	0.3281(1)	0.3159(3)	0.9344(1)	0.081(2)
C11d	0.3260(1)	0.4511(3)	0.9677(1)	0.086(2)
C12d	0.3373(1)	0.3414(3)	0.9603(1)	0.089(2)
C13d	0.3354(1)	0.4789(5)	0.9946(1)	0.135(2)
C14d	0.3578(1)	0.2626(4)	0.9802(1)	0.141(3)
Sn1e	0.09401(2)	0.57006(4)	0.71640(1)	0.0457(1)
Cl1e	0.2133(1)	0.5799(2)	0.7181(1)	0.063(1)
O1e	-0.0206(1)	0.5395(2)	0.7123(1)	0.057(1)
C21e	0.0726(1)	0.5753(2)	0.6745(1)	0.053(3)
C22e	0.0934(2)	0.6614(3)	0.6610(1)	0.089(3)
C23e	0.0794(3)	0.6654(4)	0.6337(1)	0.111(4)
C24e	0.0445(2)	0.5835(4)	0.6195(1)	0.085(3)
C25e	0.0234(2)	0.4976(4)	0.6324(1)	0.077(3)
C26e	0.0374(2)	0.4935(3)	0.6598(1)	0.067(2)
C31e	0.1025(1)	0.4309(2)	0.7413(1)	0.053(3)
C32e	0.1315(2)	0.3359(3)	0.7349(1)	0.069(2)
C33e	0.1373(2)	0.2450(3)	0.7513(1)	0.088(3)
C34e	0.1142(2)	0.2481(4)	0.7742(1)	0.090(4)
C35e	0.0854(2)	0.3411(4)	0.7809(1)	0.083(3)
C36e	0.0796(2)	0.4320(3)	0.7645(1)	0.065(2)
C41e	0.0873(1)	0.7208(2)	0.7368(1)	0.048(2)
C42e	0.1328(2)	0.8025(3)	0.7373(1)	0.059(2)
C43e	0.1286(2)	0.9000(3)	0.7505(1)	0.076(2)
C44e	0.0789(2)	0.9170(3)	0.7634(1)	0.082(3)
C45e	0.0334(2)	0.8374(4)	0.7633(1)	0.078(3)
C46e	0.0376(2)	0.7398(3)	0.7500(1)	0.061(2)
N1e	-0.1019(1)	0.5065(3)	0.7530(1)	0.072(2)
C2e	-0.1153(2)	0.5995(3)	0.7640(1)	0.102(2)
C3e	-0.1201(2)	0.6072(4)	0.7907(1)	0.128(2)
C4e	-0.1106(2)	0.5155(5)	0.8058(1)	0.118(2)
C5e	-0.0861(2)	0.3184(4)	0.8100(1)	0.106(2)
C6e	-0.0736(2)	0.2250(4)	0.7991(1)	0.108(3)
C7e	-0.0541(2)	0.1237(3)	0.7600(1)	0.124(3)
C8e	-0.0503(2)	0.1229(4)	0.7341(1)	0.134(3)
C9e	-0.0608(2)	0.2215(4)	0.7198(1)	0.105(2)
N10e	-0.0742(1)	0.3148(3)	0.7306(1)	0.073(2)
C11e	-0.0925(1)	0.4155(3)	0.7681(1)	0.064(2)
C12e	-0.0780(1)	0.3152(3)	0.7564(1)	0.065(2)
C13e	-0.0965(1)	0.4173(4)	0.7950(1)	0.086(2)
C14e	-0.0680(1)	0.2196(3)	0.7719(1)	0.089(2)

$^{*}U_{eq}$ is defined as one-third the trace of the $\mathbf{U}_{ij}$ tensor.

in using symmetrized parameters defined by modulation vectors since all orders of satellites were well observed. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 2.

Modulation functions could have been used to describe individual atom parameters but this is not a necessity. The concept of linear independence allows a multitude of choices for variables, provided they all span the same space. Modulation functions have the advantage that certain variables are associated with certain index conditions for their major contribution to observed intensities, but reflections with $2h + l = 5N \pm 1$ and $5N \pm 2$ had reasonably similar intensities, excluding the simple use of modulation functions as a basis for constrained refinement. We assumed that local object constraints were the most appropriate way of reducing the number of variables while maintaining the essential features of the structure. This allowed 524 degrees of freedom rather than the maximum 35 x 5 x 9 = 1575 for the 35 non-hydrogen atoms in the formula unit.

In the final refinement cycle, the change to the predicted sum of weighted residuals was found to be small although some shift/sigma values were still large (up to 0.5). This is a consequence of using highly correlated parameters, (rather than eigen functions of the least squares matrix) one at a time, evaluating the σ-values from the diagonal elements of the inverse of the least-squares matrix. The final difference Fourier map had peaks in the -0.90 to 1.00 eÅ^{-3} range. Selected bond dimensions are listed in Table 3. The unit cell contents are shown in Figure 1 (scheme).

Table 3. Selected bond distances and angles in $[(C_6H_5)_3SnCl \cdot H_2O \cdot C_{12}H_8N_2]_2$.*

Sn1a–Cl1a	2.501(2)	Sn1b–Cl1b	2.499(2)	Sn1c–Cl1c	2.504(2)	Sn1d–Cl1d	2.500(2)	Sn1e–Cl1e	2.505(2)
Sn1a–O1a	2.415(2)	Sn1b–O1b	2.415(2)	Sn1c–O1c	2.415(2)	Sn1d–O1d	2.415(2)	Sn1e–O1e	2.415(2)
Sn1a–C21a	2.104(3)	Sn1b–C21b	2.110(3)	Sn1c–C21c	2.125(3)	Sn1d–C21d	2.118(3)	Sn1e–C21e	2.124(3)
Sn1a–C31a	2.116(3)	Sn1b–C31b	2.116(3)	Sn1c–C31c	2.125(3)	Sn1d–C31d	2.117(3)	Sn1e–C31e	2.121(3)
Sn1a–C41a	2.131(3)	Sn1b–C41b	2.137(3)	Sn1c–C41c	2.137(3)	Sn1d–C41d	2.142(3)	Sn1e–C41e	2.144(3)
Cl1a–Sn1a–O1a	169.7(1)	Cl1b–Sn1b–O1b	172.3(1)	Cl1c–Sn1c–O1c	175.1(1)	Cl1d–Sn1d–O1d	172.9(1)	Cl1e–Sn1e–O1e	173.1(1)
Cl1a–Sn1a–C21a	90.4(1)	Cl1b–Sn1b–C21b	93.6(1)	Cl1c–Sn1c–C21c	94.9(1)	Cl1d–Sn1d–C21d	94.8(1)	Cl1e–Sn1e–C21e	92.4(1)
Cl1a–Sn1a–C31a	92.6(1)	Cl1b–Sn1b–C31b	93.5(1)	Cl1c–Sn1c–C31c	94.0(1)	Cl1d–Sn1d–C31d	92.6(1)	Cl1e–Sn1e–C31e	93.1(1)
Cl1a–Sn1a–C41a	97.9(1)	Cl1b–Sn1b–C41b	96.1(1)	Cl1c–Sn1c–C41c	96.1(1)	Cl1d–Sn1d–C41d	96.1(1)	Cl1e–Sn1e–C41e	96.1(1)
O1a–Sn1a–C21a	84.8(1)	O1b–Sn1b–C21b	80.2(1)	O1c–Sn1c–C21c	82.0(1)	O1d–Sn1d–C21d	82.1(1)	O1e–Sn1e–C21e	84.8(1)
O1a–Sn1a–C31a	83.2(1)	O1b–Sn1b–C31b	86.4(1)	O1c–Sn1c–C31c	84.8(1)	O1d–Sn1d–C31d	84.3(1)	O1e–Sn1e–C31e	83.8(1)
O1a–Sn1a–C41a	92.4(1)	O1b–Sn1b–C41b	90.8(1)	O1c–Sn1c–C41c	88.7(1)	O1d–Sn1d–C41d	91.0(1)	O1e–Sn1e–C41e	90.8(1)
C21a–Sn1a–C31a	127.7(1)	C21b–Sn1b–C31b	124.7(1)	C21c–Sn1c–C31c	124.9(1)	C21d–Sn1d–C31d	127.3(1)	C21e–Sn1e–C31e	128.2(1)
C21a–Sn1a–C41a	116.2(1)	C21b–Sn1b–C41b	116.8(1)	C21c–Sn1c–C41c	116.8(1)	C21d–Sn1d–C41d	116.5(1)	C21e–Sn1e–C41e	117.0(1)
C31a–Sn1a–C41a	115.1(1)	C31b–Sn1b–C41b	116.8(1)	C31c–Sn1c–C41c	116.1(1)	C31d–Sn1d–C41d	114.4(1)	C31e–Sn1e–C41e	113.5(1)

Intradimer contacts

O1a···N1a	3.241(4)	O1b···N1b	2.833(4)*	O1c···N1c	2.860(4)*	O1d···N1d	2.938(4)*	O1e···N1e	3.000(4)*
O1a···N10a	3.030(4)*	O1b···N10b	3.566(4)	O1c···N10c	3.604(4)	O1d···N10d	3.368(4)	O1e···N10e	3.190(4)
O1a···N1a[i]	3.073(4)*	O1b···N1e[ii]	3.131(4)*	O1c···N1d[i]	2.940(4)*	O1d···N1c[i]	3.299(4)	O1e···N1b[ii]	3.382(4)
O1a···N10a[i]	3.173(4)	O1b···N10e[ii]	3.205(4)	O1c···N10d[i]	3.131(4)	O1d···N10c[i]	2.816(4)*	O1e···N10b[ii]	2.780(4)*

[i] Symmetry transformation: $i = 1-x, 1-y, 1-z$; $ii = -x, 1-y, 1-z$.
*Hydrogen bond
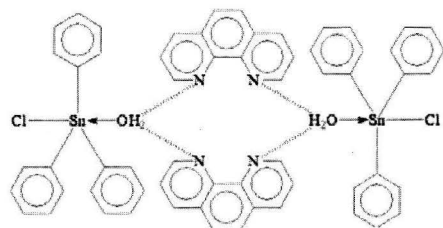
Scheme 1. Bis(aquachlorotriphenyltin.1,10-phenanthroline).
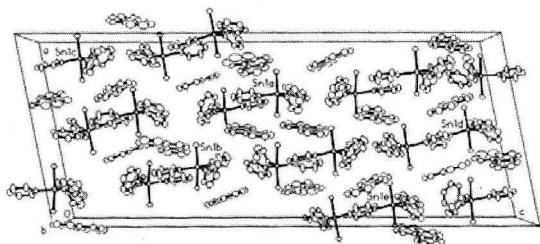
Figure 1. Projection of the cell contents down the **b**-axis. Labels a, b, c, d and e distinguish pseudo translationally-related molecules. Hydrogen bonds are not shown.

RESULTS AND DISCUSSION

For the $P2_1/n$ cell, the reflections can be indexed as $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ or $h_0\mathbf{a}_0^* + k_0\mathbf{b}_0^* + l_0\mathbf{c}_0^* + m_0\mathbf{q}$ where $\mathbf{a}_0^* = \mathbf{a}^* + 3\mathbf{c}^*$, $\mathbf{b}_0^* = -\mathbf{b}^*$, $\mathbf{c}_0^* = \mathbf{a}^* - 2\mathbf{c}^*$; the values for the indices depend on the choice of $\mathbf{q}$. If $\mathbf{q} = \mathbf{c}^* = (\mathbf{a}_0^* - \mathbf{b}_0^*)/5$, then $h_0 = h - N$, $k_0 = -k$, $l_0 = N$, $m_0 = -3h + l + 5N$, where N is any integer which can be chosen so that m_0 lies in the -2 to +2 range. The n-glide special reflection condition of $h + l$ even for the $h0l$ reflections now corresponds to $l_0 + m_0$ even for the $h_0 0 l_0 m_0$ reflections, but this does not correspond to a standard setting for a (3+1)-dimensional superspace group number 14.1 in Table 9.8.3.5, Section 9.8 of the *International Tables for Crystallography*, Volume C [16]. However, if we let $\mathbf{q} = \mathbf{c}^* + \mathbf{c}_0^* = \mathbf{a}^* - \mathbf{c}^* = (\mathbf{a}_0^* + 4\mathbf{c}_0^*)/5$, then $h_0 = N$, $k_0 = -k$, $l_0 = -h - l + 4N$, $m_0 = 2h + l - 5N$, where N is any integer. The n-glide special reflection condition ($h + l$ even for $h0l$ reflections) now corresponds to l_0 even for $h_0 0 l_0 m_0$ reflections. This is seen to correspond to swapping $\mathbf{b}$ for $\mathbf{c}$ in the (3+1)-dimensional superspace group number 14.1. We can therefore describe the (3+1)-dimensional superspace group as $P2_1/c(\alpha0\gamma)$ with $\alpha = 1/5$, $\gamma = 4/5$ and symmetry elements $(\mathbf{1}, 1 \mid 0, 0, 0, 0)$, $(\mathbf{m}, 1 \mid 0, 1/2, 1/2, 0)$, $(\mathbf{-1}, -1 \mid 0, 0, 0, \tau_4)$, $(\mathbf{2}, -1 \mid 0, 1/2, 1/2, \tau_4)$ with $\tau_4 = 0$ if we wish to have a true center of inversion at the origin.

A (3+1) dimensional superspace group is described by operators $(\mathbf{R}_j, \varepsilon_j \mid \tau_{j1}, \tau_{j2}, \tau_{j3}, \tau_{j4})$ or $(\mathbf{R}_j, \varepsilon_j \mid \tau_j, \tau_{j4})$ where $\mathbf{R}_j$ is a 3-dimensional symmetry operator with an associated 3-dimensional translation $\mathbf{t}_j = \tau_{j1}\mathbf{a}_0 + \tau_{j2}\mathbf{b}_0 + \tau_{j3}\mathbf{c}_0$. Allowed values of $\mathbf{R}_j$ satisfy the condition that $\mathbf{R}_j\mathbf{q} = \varepsilon_j\mathbf{q} + \mathbf{g}_0$ where $\varepsilon_j = \pm1$ and $\mathbf{g}_0$ is a Bragg reflection of the parent structure.

There is a choice of global phase φ associated with a modulated structure corresponding to a translation of the crystal contents by $(\mathbf{1}, 1 \mid 0, 0, 0, \varphi)$. This leaves unchanged symmetry elements with $\varepsilon_j = 1$ but changes the value of τ_{4j} to $\tau_{4j} - 2\varphi$ for symmetry elements with $\varepsilon_j = -1$. This is analogous, for example, to changing the 3-dimensional symmetry elements $x, -y, z$ and $x, y, -z+1/3$ to $x, -y, z$ and $x, y, -z$ by translating the unit cell contents by 0,0,1/6.

We can describe the scattering density of a (3+1)-dimensional incommensurate crystal structure as

$\Sigma_m \rho_m(\mathbf{r})$ where $\rho_m(\mathbf{r})$ is the Fourier transform of the mth subset of reflections $\{F_m(\mathbf{H})\}$, where $\mathbf{H} = \mathbf{G}_o + m\mathbf{q}$ and $\mathbf{G}_o$ is any Bragg reflection of the parent structure. When a (3+1)-dimensional operator $(\mathbf{R}_j, \varepsilon_j \mid \mathbf{t}_j, \tau_{j4})$ operates on $\rho(\mathbf{r})$, we change $F(\mathbf{H})$ to exp $[2\pi i(h\tau_{j1} + k\tau_{j2} + l\tau_{j3} + m\tau_{j4})]F(\mathbf{HR}_j)$ and so $(\mathbf{1}, 1 \mid 0, 0, 0, \varphi)$ operating on the cell contents changes $\rho_m(\mathbf{r})$ to $\exp(2\pi i m\varphi)\rho_m(\mathbf{r})$ and any value of $F_m(\mathbf{H})$ to $\exp(2\pi i m\varphi)F_m(\mathbf{H})$. For real scattering density, $\rho_{-m}(\mathbf{r}) = \rho_m(\mathbf{r})^*$ and $F(\mathbf{-H}) = F(\mathbf{H})^*$.

The consequences of the structure being commensurate

When a structure is commensurate, $N\mathbf{q} = N_1\mathbf{a}_o{}^* + N_2\mathbf{b}_o{}^* + N_3\mathbf{c}_o{}^*$, where N, N_1, N_2 and N_3 are integers and we can write $\mathbf{H} = (h - nN_1)\mathbf{a}_o{}^* + (k - nN_2)\mathbf{b}_o{}^* + (l - nN_3)\mathbf{c}_o{}^* + (m + nN)\mathbf{q}$, where n is any integer. Consequently, $F(\mathbf{H})$ becomes $\Sigma_n F_{m+nN}(\mathbf{H})$ and reflections related by (3+1) dimensional symmetry elements now have the relationship $\Sigma_n F_{m+nN}(\mathbf{H}) = \Sigma_n \exp[2\pi i\Phi_{nj}(\mathbf{H})]F_{e(m+nN)}(\mathbf{HR}_j)$, where $\Phi_{nj}(\mathbf{H}) = (h - nN_1)\tau_{j1} + (k - nN_2)\tau_{j2} + (l - nN_3)\tau_{j3} + (m + nN)\tau_{j4}$.

Equivalence of reflection intensities, and hence the true maintenance of a (3+1) dimensional symmetry element, can only occur if $\exp[2\pi i(N_1\tau_{j1} + N_2\tau_{j3} + N_3\tau_{j3} - N\tau_{j4})]$ is exactly 1.0. For our system, $N = 5$, $N_1 = 1$, $N_2 = 0$ and $N_3 = 4$, so that this condition is always satisfied for $(\mathbf{1}, 1 \mid 0, 0, 0, 0)$ and $(\mathbf{m}, 1 \mid 0, 1/2, 1/2, 0)$, but is only satisfied for $(\mathbf{-1}, -1 \mid 0, 0, 0, \tau_4)$ and $(\mathbf{2}, -1 \mid 0, 1/2, 1/2, \tau_4)$ if τ_4 is an integer multiple of 1/5. The options simply correspond to having alternative origins.

Alternative origins that do not change the symmetry elements

We can have alternative origins for a structure in three dimensions without changing the symmetry elements or the magnitudes of structure factors, i.e., we can make certain translations of the cell contents without changing the phase relationships between equivalent reflections. For example, translations by $\mathbf{a}/2$, $\mathbf{b}/2$ or $\mathbf{c}/2$ of the contents of a $P2_1/c$ structure change the phases of reflections but not the relationships between equivalent reflections. Likewise, a translation in (3+1) dimensional space using the operator $(\mathbf{1}, 1 \mid 0, 0, 0, 1/2)$ leaves values of τ_{4j}, modulo 1, unchanged but changes values of $F_m(\mathbf{H})$ to $(-1)^m F_m(\mathbf{H})$. This is of no consequence if the structure is incommensurate but must be considered when $(2M+1)\mathbf{q} = \mathbf{g}_o$, a Bragg reflection of the parent structure.

We now have a number of possible commensurate structures derived from the same incommensurate prototype, differing only in the choice of global phase corresponding to a translation of the crystal contents by $(\mathbf{1}, 1 \mid 0, 0, 0, j)$ to give structure factors $F(\mathbf{H}) = \Sigma_n \exp[2\pi i(m+nN)\varphi]F_{m+nN}(\mathbf{H})$.

We can consider only those terms with the two smallest values of $|m+nN|$, and choose $\varphi = 0$ to correspond to having a true center of inversion at the origin. Then, as φ varies, we obtain $|F(\mathbf{H})|^2 = |F'(\mathbf{H})|^2 + |F''(\mathbf{H})|^2 + \cos(2\pi N\varphi)[F'(\mathbf{H})^*F''(\mathbf{H}) + F'(\mathbf{H})F''(\mathbf{H})^*]$ with $N = 5$. The $\cos(2\pi N\varphi)$ factor is 1.0 when $\varphi = 0$, -1.0 when $\varphi = 1/2$ and 0.0 when $\varphi = 1/4$. In there was no anomalous scattering $F'(\mathbf{H})$ and $F''(\mathbf{H})$ would both be real. If the structure is truly incommensurate but intensities accidentally overlap, then we obtain intensities that effectively are indistinguishable from those obtained for the commensurate $\varphi = 1/4$ case, which has space group Pn and has $\exp[2\pi i(m+nN)\varphi]$ real if $m+nN$ is even and imaginary if $m+nN$ is odd. Intensities for the $\varphi = 0$ and $\varphi = 1/2$ cases would then fit equally badly. However, if the $\varphi = 0$ case is correct, then the $\varphi = 1/2$ case fits twice as badly as does the $\varphi = 1/4$ case.

We determined the crystal structure by using standard 3-dimensional methods, and then refined the $P2_1/n$ structure by using constrained refinement techniques. Our first solution corresponded to the worst scenario. We obtained an initial model for the best scenario by simply multiplying calculated structure factors by -1.0 for of all $m = \pm1$ reflections and then re-determining the structure from the resulting Fourier map using the same $P2_1/n$ symmetry elements.

Atom labeling and structure description

When a (3+1)-dimensional operator $(\mathbf{R}, \varepsilon \mid \mathbf{t}, \tau_4)$ operates on $\rho(\mathbf{r})$, we change $F_m(\mathbf{H})$ to $\exp[2\pi i(h\tau_1 + k\tau_2 + l\tau_3 + m\tau_4)]F_{\varepsilon m}(\mathbf{HR})$, which does not change in value when the values of the τ_n are changed by any integer. This requires that the operator changes $\rho_m(\mathbf{r})$ to $\exp[2\pi i m(\tau_4 - \mathbf{q}.\mathbf{t})]\rho_{\varepsilon m}(\mathbf{Rr} + \mathbf{t})$.

For our structure, $\mathbf{q} = (\mathbf{a}_o{}^* + 4\mathbf{c}_o{}^*)/5 = \mathbf{a}^* - \mathbf{c}^*$. The asymmetric unit contains five $(C_6H_5)_3SnCl \cdot H_2O$ and five $C_{12}H_8N_2$ entities. Atoms whose labels end in a are in molecules closest to the true inversion at $(1/2, 1/2, 1/2)$ for the cell $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. Pseudo translation relates the molecules in the asymmetric unit. The remaining atoms are related by the pseudo translations $(\mathbf{1}, 1 \mid -\mathbf{a}_o, 0)^n = (\mathbf{1}, 1 \mid -n\mathbf{a}_o, 0)$, $n = 1,2,3,4$ and are distinguished by the b, c, d and e labels, respectively. The smallest

phase shifts for the primary modulation wave associated with $\pm\mathbf{q}$ are associated with the sequence $[a — b — c — d — e]$. The sequence $[a — c — e — b — d]$ etc., shows the smallest phase shifts for the modulation wave associated with $\pm 2\mathbf{q}$.

The use of the operators $(\mathbf{m}, 1 \mid \mathbf{c}_o/2, 0)^n = (\mathbf{m}^n, 1 \mid n\mathbf{c}_o/2, 0)$, $n = 0$ to 9, creates the sequence $[a — c' — e — b' — d — a' — c — e' — b — d' —]$ where the molecules that are five apart in the sequence are related by the true glide operation, $(\mathbf{m}, 1 \mid 5\mathbf{c}_o/2, 0)$.

The close contacts between the oxygen atoms of the coordinated water molecule and the nitrogen atoms of the 1,10-phenanthroline heterocycle (Table 2) reveal the evolution of the title compound as hydrogen-bonded dimers (Fig. 2). The i and ii labels denote a true inversion. There are two shortest contacts for each water molecule to the nitrogen atoms belonging to different heterocycles. We also note that

the evolution with pseudo translation for labels obtained by using the $\varepsilon = -1$ operations is in the reverse sequence to that applying to the other atoms. There are also possible interactions about other pseudo inversion centers, and atoms whose labels end in d are closest to the true inversion at 0, 1/2, 1/2. We also note the evolution of interactions about the pseudo screw axis. Molecules nearest the true screw axis at 1/4, y, 1/4 have labels that end in b for the aquachlorotriphenyltin moiety but end in e for the 1,10-phenanthroline moiety, whereas molecules nearest the true screw axis at 1/4, y, 3/4 have labels that end in e for the organotin moiety but end in c for the heterocycle.
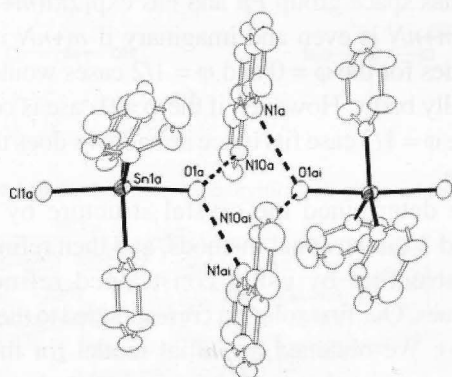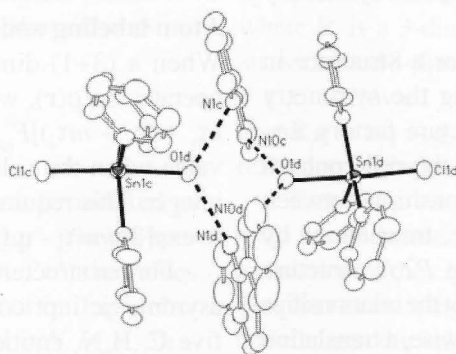
Figure 2a. *ORTEP* plot of the centrosymmetric ($1 - x$, $1 - y$, $1 - z$) hydrogen-bonded a dimer at the 30% probability level when viewed down the **b**-axis.
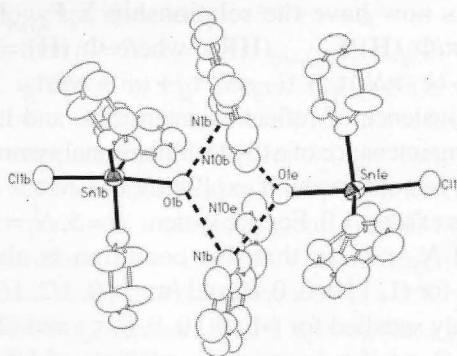
Figure 2b. *ORTEP* plot of the hydrogen-bonded b molecule and the symmetry-transformed ($-x$, $1 - y$, $1 - z$) e molecule at the 30% probability level when viewed down the **b**-axis. Hydrogen atoms are not shown.

Figure 2c. *ORTEP* plot of the hydrogen-bonded c molecule and the symmetry-transformed ($1 - x$, $1 - y$, $2 - z$) e molecule at the 30% probability level when viewed down the **b**-axis. Hydrogen atoms are not shown.

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