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Short communication

CRYSTAL STRUCTURE OF TRIPHENYL(QUINOLIN-8-OLATO)TIN(IV)

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Triphenyl(quinolin-8-olato)tin crystallizes as two symmetry-independent molecules whose metal atoms both exist in a *cis*-C_3SnNO trigonal bipyramidal coordination polyhedron that is 29 % distorted toward a square pyramid. The crystal structure [orthorhombic *Pbcn* space group], with *a* 26.701(2), *b* 10.3555(6), *c* 31.322(2) Å; *V* 8660.5(9) Å^3] is refined from 5950 $I > 2\sigma(I)$ Mo–$K\alpha$ reflections measured at 200 K to an *R*-index of 0.050.

Key words: triphenyl(quinolin-8-olato)tin; crystal structure

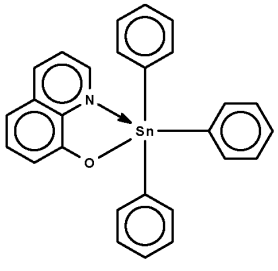
КРИСТАЛНА СТРУКТУРА НА ТРИФЕНИЛ(ХИНОЛИН-8-ОЛАТО)КАЛАЈ(IV)

Трифенил(хинолин-8-олато)калај кристализира како две симетриски независни молекули, каде што обата метални атома се наоѓаат во *cis*-C_3SnNO тригонално-бипирамидален координационен полиедар кој е 29 % деформиран спрема квадратна пирамида. Кристалната структура [орторомбична *Pbcn* просторна група], каде *a* = 26,701(2), *b* = 10,3555(6), *c* = 31,322(2) Å; *V* = 8660,5(9) Å^3] е уточнета од 5950 $I > 2\sigma(I)$ Mo–$K\alpha$ рефлекси определени на 200 K со *R*-индекс од 0,050.

Клучни зборови: трифенил(хинолин-8-олато)калај(IV), кристална структура

1. INTRODUCTION

The synthesis of the triphenyltin(IV) derivative of 8-hydroxyquinoline was first reported 50 years ago [1]; shortly after, the first assignment of the solid-state structure from spectroscopic techniques then available were published [2–5]. The assignment was later augmented by tin-119*m* Mössbauer measurements [6–11]. Since then, the structure has also been interpreted on the basis of high-resolution solid-state tin-119 NMR [12]. Although the point-charge model from Mössbauer measurements implicated a *cis*-C_3SnNO trigonal bipyramidal geometry [13], definitive proof has been unavailable, probably because of the compound typically precipitate from solution as a microcrystalline powder. In a recent attempt to corroborate the assignment, the crystal structures of four 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olato derivatives were investigated. Thereby, it was assumed that the substitutents in the anionic ligand should not perturb the geometry of the metal center. However, three were found to adopt a square pyramidal geometry and the fourth a trigonal bipyramidal geometry [14]. The use of *t*-butanol as solvent for purification in this study has led to the isolation of single crystals, and consequently, a final resolution of the structure of triphenyl(quinolin-8-olato)tin (Scheme I).



Scheme 1

2. EXPERIMENTAL

Methoxytriphenyltin was synthesized from triphenyltin chloride and sodium methoxide. This reagent (0.764 g, 2 mmol) and 8-hydroxyquinoline (0.29 g, 2 mmol) were heated in methanol (20 ml) for 2 hours. The solvent was removed under reduced pressure and the solid recrystallized from *t*-butanol to give yellow crystals, m.p. 412–413 K. ^{119}Sn NMR in $CDCl_3$: – 173 ppm.

Diffraction measurements were performed at 200 K with a 0.35×0.30×0.08 specimen on a Stoe Imaging Plate diffractometer [15]. The structure was solved by direct phase determination and refined [16] to an *R*-index of 0.05 for 5950 $I \geq 2\sigma(I)$ reflection. The structure is depicted [17] as a thermal ellipsoid plot in Fig. 1. The details of the crystal structure in CIF format are deposited with the Cambridge Structural Database Centre as CCDC 745603.

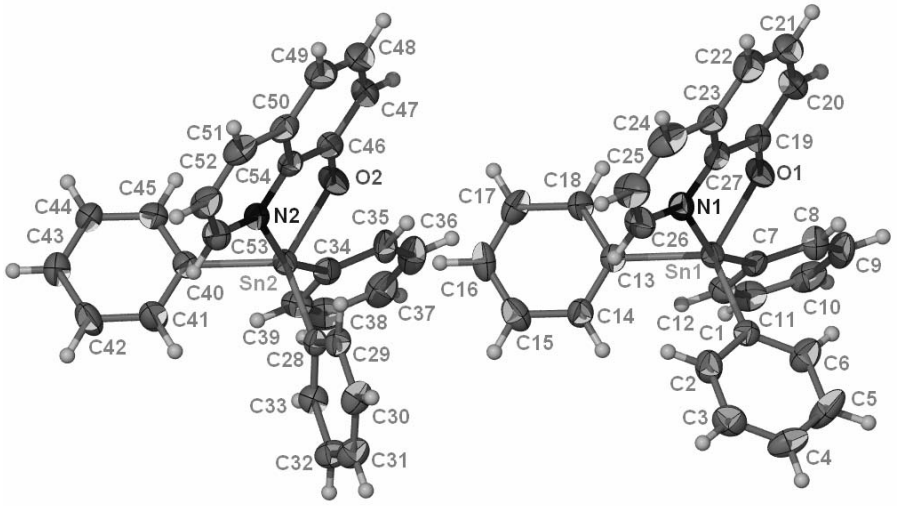


Fig. 1. Molecular structure of the two independent molecules of triphenyl(quinolin-8-olato)tin.
Selected bond distances and angles: Sn1–O1 2.057(3), Sn1–N1 2.472(4), Sn1–C1 2.147(5), Sn1–C7 2.160(5), Sn1–C13 2.163(5), Sn2–C28 2.145(4), Sn2–C34 2.157(5), Sn2–C40 2.168(5), Sn2–O2 2.058(3), Sn2–N2 2.444(4) Å; O1–Sn1–C1 116.7(2), O1–Sn1–C7 87.5(2), O1–Sn1–C13 122.3(2), O1–Sn1–N1 71.5(1), N1–Sn1–C1 88.6(2), N1–Sn1–C7 158.7(2), N1–Sn1–C13 82.5(2), C1–Sn1–C7 104.7(2), C1–Sn1–C13 112.9(2), C7–Sn1–C13 106.6(2), O2–Sn2–C28 118.4(2), O2–Sn2–C34 87.8(2), O2–Sn2–C40 122.9(2), O2–Sn2–N2 71.7(1), N2–Sn2–C28 87.5(2), N2–Sn2–C34 159.4(2), N2–Sn2–C40 84.3(2), C28–Sn2–C34 104.6(2), C28–Sn2–C40 111.2(2), C34–Sn2–C40 106.0(2) °

3. RESULTS AND DISCUSSION

Triphenyl(quinolin-8-olato)tin crystallizes as two symmetry-independent molecules having the metal atom in a coordination geometry better described as a *cis*-C_3SnNO trigonal bipyramid (tbp) that is distorted towards a square pyramid (sqp) (Fig. 1). The Sn–C distances C–C–C angles fall in a narrow range [2.145(4) to 2.168(5) Å, 104.6(2) to 112.9(2) °]. The Sn–C_{axial} distances are not significantly longer than the Sn–$C_{equatorial}$ distances; however, the axial Sn–N bonds are much longer, and the tin atoms are displaced out of the equatorial planes in the direction of the axial carbon atoms. For both molecules, the tbp–sqp Berry pseudorotation pathway as calculated by *PLATON* [18] on the basis of dihedral angles [19] is 29 % displaced towards a square pyramid (C1 and C28 are the pivot atoms). One of the axial sites is occupied by the nitrogen atom of the ligand; the small bite results in a somewhat longer tin-nitrogen bond as well as a bent nitrogen–tin–nitrogen skeleton. In contrast, the quinolin-8-thiolato derivative [20] is less distorted towards a square pyramid (14 %). Similarly, the distortion (18 %) is also less for triphenyl(propane-1,3-dionato)tin, which features a six-membered chelate ring [21]. For the bis-chelated diorganotin derivatives of 8-hydroxyquinoline [22–27], a similar bite angle is noted; however, the corresponding bond is shorter owing to decreased crowding in an octahedral coordination sphere.

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