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Preliminary communication

THE STRUCTURE OF NITRATOTRIPHENYLSTANNYLTIN(II): A COMPOUND WITH A TIN(IV)—TIN(II) BOND

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Summary

A compound of formula $[Sn^{II}(NO_3)\{(C_6H_5)_3Sn^{IV}\}]$, containing a tin(IV)—tin(II) bond, has been prepared, and its crystal structure is determined.

This work was undertaken as a part of a systematic study of the structural properties of organotin compounds containing the nitrate group as ligand [1-3].

From the reaction of diphenyltin(IV) dinitrate and triphenylarsine (molar ratio 1/1), under nitrogen atmosphere and in dry acetone, a microcrystalline white product was isolated. Recrystallization from acetone—chloroform gave colourless crystals with analytical and spectroscopic properties different from those of the microcrystalline product. The crystal structure of the recrystallized product is described (a study of the initial product, which has not yet been identified, is in progress in our laboratory).

The crystals are monoclinic (space group $P2_1/c$) with a = 10.409(5), b = 18.896(7), c = 9.122(5) Å, β = 98.3(1)°, Z = 4. The X-ray structure was determined from diffractometer data (Mo-K_α radiation, 2686 independent reflections) using Patterson and Fourier methods and refined by means of block-diagonal least-squares down to R = 10.4%.

The molecular structure of the complex is depicted in Fig. 1. The major feature of interest is that this is the first example of a compound, in which a tin(IV)—tin(II) bond has been shown to be present by an X-ray structural study. This bond is much shorter (2.475 Å) than the sum of Pauling's covalent radii (2.80 Å) [4] and than the value of 2.69 Å observed by Bandoli et al. for a tin(IV)—tin(IV) bond in di-μ-acetatobis(diphenyltin) [5].

The environment of tin(IV) is approximately tetrahedral and involves, in addition to tin(II), the three phenyl rings at 1.90, 1.93, 1.97 Å. These distances are significantly shorter than the Sn^{IV}—C(phenyl) bonds for four-coordinated tin, which fall in the range 2.07-2.19 Å [6]. This unusual shortening may be due to π-interactions involving the aromatic rings and the

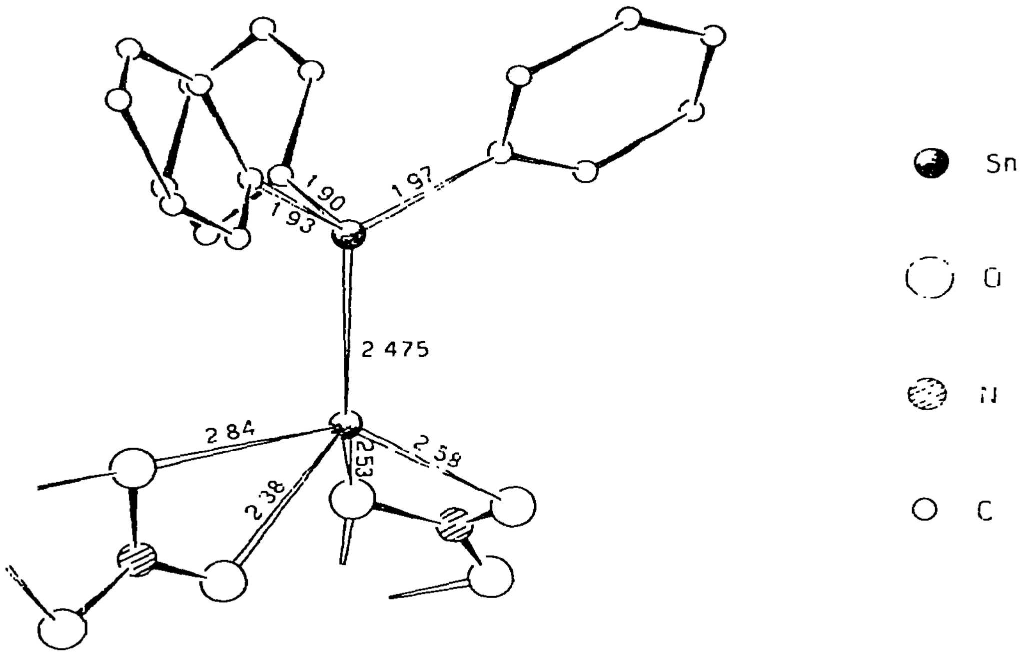

Fig.1. Structure of the complex with bond distances in the two coordination polyhedra.

atomic orbitals of the two tin atoms.

The tin(II) atom is five-coordinated, in a highly irregular way (the angles are varying from 47.3 to 144.4°), by the triphenylstannyl moiety via tin and by four oxygen atoms from two adjacent nitrate groups. It is noteworthy that a sixth loose contact of 2.96 Å exists between tin(II) and a carbon atom from a phenyl ring of an adjacent molecule.

The behaviour of the nitrate group in coordinating to tin(II) is rather unusual, as it bridges two tin(II) atoms through two bidentate contacts, with all the oxygen atoms involved in coordination. Such behaviour resembles that observed by us in 2-aminobenzothiazolatonitratotin(II) [3], but does not fall within the classification proposed by Addison et al. [7], as it involves two more oxygen—metal contacts than are involved in their *anti—anti* bridging structures. This bridging behaviour of the nitrate group generates zig-zag chains running along the *z* axis.

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