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Preliminary communication

A TETRANUCLEAR METAL SYSTEM IN NITRATOTRIS(TRIPHENYLSTANNYL)TIN(IV)

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Summary

A new organotin nitrato compound of formula $[\mathrm{Sn^{IV}(NO_3)\{(C_6H_5)_3Sn^{IV}\}_3}]$, has been obtained and its crystal structure is reported; this represents the first X-ray characterization of a tetranuclear system of tin atoms.

As a part of a programme of structural researches on organotin derivatives containing the nitrate group as ligand [1-4], the title compound was prepared and its X-ray crystal structure was determined. It represents the first case of a tetranuclear organotin compound studied by X-ray diffraction.

White tabular crystals were obtained from the reaction of tris(dimethylsulphoxide)nitratodiphenyltin(IV) nitrate (whose chemical and structural properties have been already described [2]) with triphenylarsine, under nitrogen in dry acetone. Recrystallization was from acetone—chloroform.

The compound crystallizes in the space group $P2_1/n$* with four molecules in a unit-cell of dimensions: a = 19.153(8), b = 13.957(6), c = 17.914(8) Å, β = 95.8(1)°. From a total of 8404 independent reflections, measured by diffractometer methods with Mo-K_α radiation (λ = 0.7107 Å) up to θ = 25°, 4372, being found statistically above the background, were used in the analysis. This was carried out using the heavy-atom technique and block-diagonal least-squares (anisotropic thermal parameters for the tin atoms, isotropic thermal parameters for the remaining 58 atoms) down to conventional R = 0.098. No attempts for localizing the hydrogen atoms were made.

As shown in the diagrammatic projection (Fig. 1) the structure consists of three triphenylstannyl groups bound via the metals to a fourth tin atom, Sn(4). Coordination around this atom also involves the nitrate group, which acts as a "symmetrically bidentate" ligand [5], so that the central metal atom shows pentacoordination. The tetranuclear system formed by the tin atoms shows a

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*Equivalent positions: x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$.

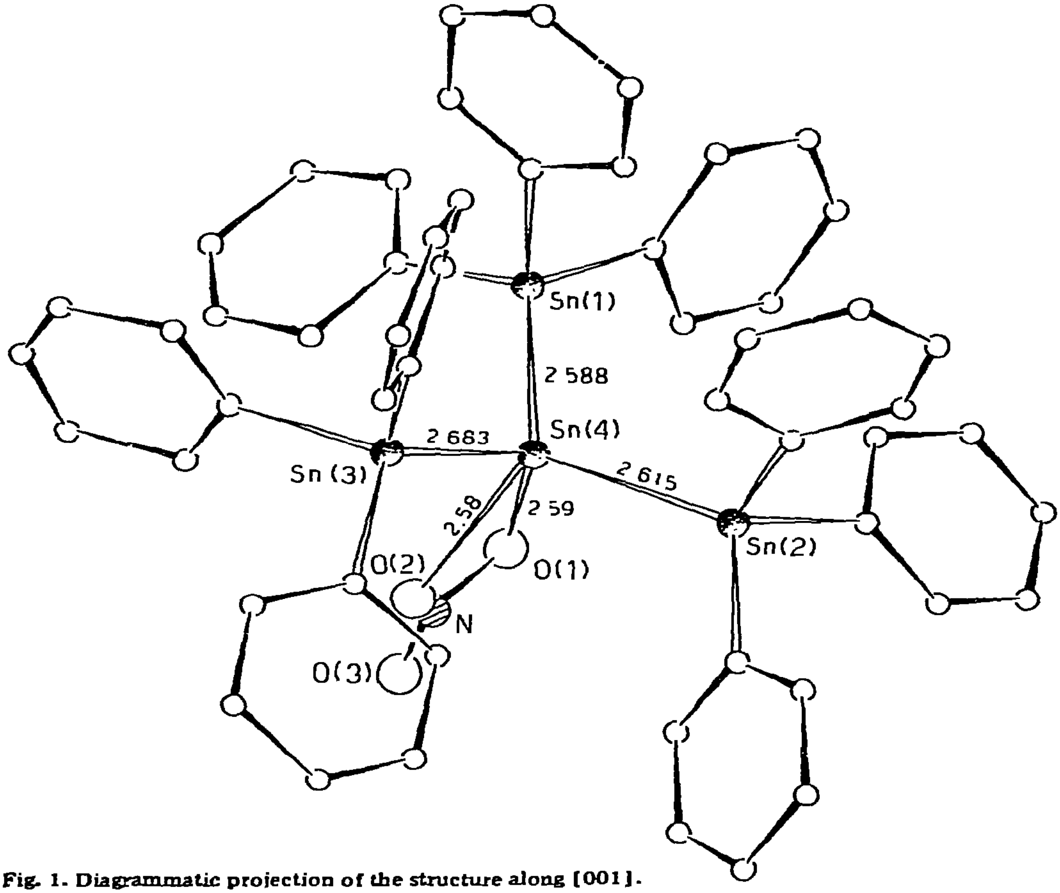

Fig. 1. Diagrammatic projection of the structure along [001].

flattened pyramidal configuration with Sn(4) out of the Sn(1)—Sn(2)—Sn(3) plane by 0.66 Å. In this system the Sn—Sn bond distances (2.588, 2.615, 2.683 Å) are slightly shorter than that (2.69 Å) found in di-μ-acetatobis(diphenyltin) [6] and, more relevantly, shorter than those (2.780, 2.759 Å) observed in hexaphenyldistannane [7].

In the triphenylstannyl moieties the metal atoms are tetrahedral with the Sn—Sn—C angles larger (mean value 116.4°) and the C—Sn—C angles smaller (mean value 101.7°) than the theoretical tetrahedral value. The Sn—C and the C—C bond distances in them are not significantly different, their mean values being 1.96(2) Å for the former and 1.39(3) Å for the latter. The shortening of the Sn—C bonds, as compared with those usually observed in similar compounds [8], is somewhat surprising, but the same effect has been already observed in nitratotriphenylstannyltin(II) [3], whose structure can be compared with that under consideration by taking into account the different oxidation state of tin. The only significant difference between the two structures is due to the behaviour of the nitrate group which in the present compound covalently chelates to metal, while in nitratotriphenylstannyltin(II) it bridges two different metal atoms through all its three oxygen atoms.

Packing is determined by normal Van der Waals contacts.

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