

Preliminary communication

THE CRYSTAL STRUCTURE OF TETRAKIS[TRIMETHYLTHIOMETHYL-
PLATINUM(IV)], $[\text{Pt}(\text{CH}_3)_3(\text{SCH}_3)]_4$

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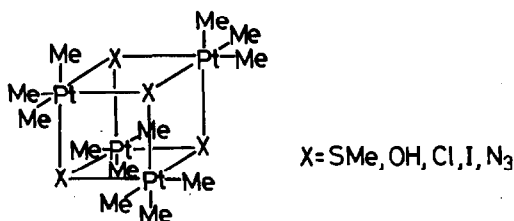
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Summary

The crystal structure of trimethyl(thiomethyl)platinum(IV), $[\text{Pt}(\text{CH}_3)_3(\text{SCH}_3)]_4$, has been determined using X-ray diffraction. The compound has three independent but isostructural tetrameric units in the asymmetric unit. The four metal atoms in each tetramer are linked by bridging thiomethyl sulphurs, with three methyl groups completing the octahedral coordination around each platinum. Mean interatomic distances within the tetramer are Pt—S, 2.48(2), Pt—C, 2.00(4), Pt—Pt, 3.80(2) Å, with a mean bridge angle S—Pt—S, 79.1(7)°.

A number of tetrameric trimethylplatinum compounds are known, having the basic 'cubane' type of structure. Hall et al. [1] reported the synthesis, infrared, Raman and proton magnetic resonance spectra on the title compound, the thiomethyl analogue. The crystal structures of the hydroxide [2—4], chloride [5], iodide [6] and azide [7] are known. We now present results of a single crystal X-ray diffraction study which confirms the tetrameric nature of the title compound.

The title compound was prepared by the procedure described in ref. 1. Large colourless crystals were recrystallised from hexane. X-ray data were collected on an irregular shaped fragment (0.20 × 0.16 × 0.10 mm), cleaved from a larger crystal, and mounted about the *b* axis. A Nicolet R3m four-circle computer-controlled diffractometer using an $\omega-2\theta$ scan technique and



graphite monochromated Mo- K_{α} radiation (λ 0.71069 Å) was used. Accurate cell parameters were obtained from least squares refinement of 15 high angle non-axial reflections. 7688 unique reflections were collected up to $2\theta_{\max} \leq 45^{\circ}$. The intensities of three standards regularly monitored during data collection indicated crystal stability. The intensity data were processed with the learnt profile fitting procedure [8] and 3711 observed reflections with $I > 3.0\sigma(I)$ were used in structure refinement. Data were corrected for absorption.

Crystal data. C₁₆H₄₈Pt₄S₄, $M = 1149.17$; monoclinic, space group $P2_1/c$, a 18.435(3), b 9.560(1), c 33.48(1) Å, β 93.63(2) $^{\circ}$, V 5888 Å³, d_{expt} 2.60 (flotation in CCl₄/CBr₄), $Z = 8$, d_{calcd} 2.593 g cm⁻³, μ (Mo- K_{α}) 194.2 cm⁻¹.

Structure determination

The measured density indicated two independent tetramers in the asymmetric unit. Four of the eight Pt atoms were located in an EES direct methods calculation (SHELX-76[9]) using three hand selected origin defining and eleven multi-solution reflections. Subsequent weighted difference-Fourier syntheses located the remaining Pt atoms about two special positions on two-fold rotational axes, together with all the remaining heavy atoms. Blocked-matrix least-squares refinement with anisotropic thermal parameters on Pt and S atoms only reduced R from 0.71 to 0.088 and $R_w = 0.092$, with $w = 1.02/(\sigma^2 F_0 + 0.008F_0^2)$. No hydrogens were included in the refinement*.

The interpretation by Hall et al. [1] of PMR and vibrational spectra in terms of a tetrameric species has been confirmed (Fig. 1). However, the crystal structure determination shows three distinct but isostructural tetramers of $[(\text{CH}_3)_3\text{Pt}(\text{SCH}_3)]_4$ in the cell. Two of these are at special positions ($\frac{1}{2}, y_1, \frac{1}{4}$ and $0, y_2, \frac{1}{4}$) with 2-fold molecular symmetry coincident with crystallographic symmetry, while the third is at a general position. The Pt and S atoms were located with a relatively high degree of certainty but the carbon atoms had significantly larger errors. This is comparable with other determinations in the literature. The reason for lack of precision could be due to errors in correcting for absorption, and possibly the dynamic nature of methyl groups, indicated by their relatively high thermal parameters.

Strictly speaking these tetramers are not represented by a cube but rather a rhombohedron with the parameters a (Pt-X distance) and α (X-Pt-X angle). The value of α is constant, while a varies according to the size of the X

*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication. Tables of bond lengths and angles, anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

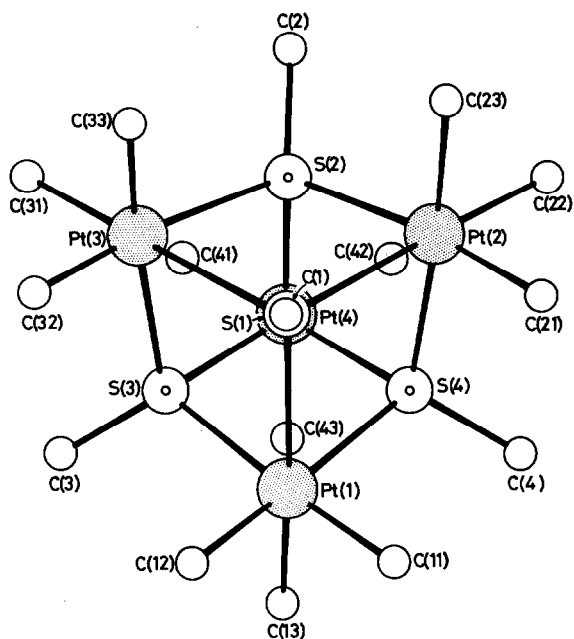


Fig. 1. Molecular configuration and atom naming scheme for $[\text{Pt}(\text{CH}_3)_3(\text{SCH}_3)]_4$, viewed down the pseudo three-fold axis.

substituent. Thus the Pt—Pt distance (Table 1) will vary according to the value of a and probably represents a very weak metal—metal interaction. Table 1 indicates that the iodide [6] is not comparable and throws some doubt on the postulated iodide parameters. The distances found for this compound were Pt—I, 2.83; Pt—Pt, 2.77 Å and I—Pt—I, 93.3°.

The packing of the tetrameric molecules in the unit cell (Fig. 2) is analogous to spherical close packing. It contains no significant intermolecular associations.

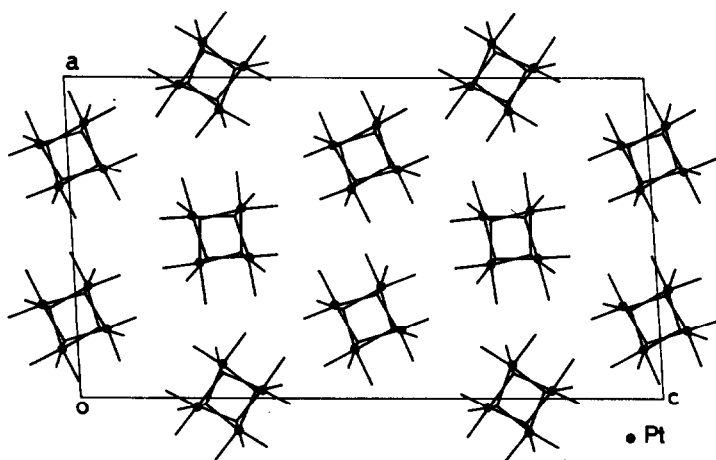


Fig. 2. Packing in the unit cell viewed down b .

TABLE 1

COMPARISON OF THE STRUCTURAL FEATURES OF TETRAMERIC PLATINUM(IV) COMPOUNDS OF THE TYPE $[(CH_3)_3PtX]_4$

	a		α	ref.
	Pt—X (Å)	Pt—Pt (Å)	X—Pt—X ($^\circ$)	
X = OH (X-ray)	2.22(1)	3.430(2)	77.6	2
X = OH (neutron)	2.20(4)	3.41(4)	78(2)	4
X = Cl	2.48	3.78	81	5
X = N ₃	2.25(6)	3.45(4)	79.2	7
X = SCH ₃	2.48(2)	3.80(2)	79.1(7)	This work

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