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Synthesis and crystal and molecular structure of a binuclear tin(IV)–squarate species

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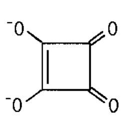
Abstract

The reaction of $SnCl_4$ with squaric acid in methanol yields colorless crystals of $[(n\text{-}C_4H_9)_4N]_2[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]$. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a=13.914(2)$, $b=10.858(3)$, $c=19.305(4)$ Å, $\beta=112.49(1)°$, $V=2694.8(12)$ Å^3, $Z=2$, $D_{calc}=1.42$ g cm^{-3}. Structure solution and refinement based on 2120 reflections with $F_o \geqslant 6\sigma(F_o)$ (Mo Kα radiation, $\lambda=0.71073$ Å, 3529 reflections collected) converged at a conventional discrepancy value of 0.069. The structure consists of discrete $(n\text{-}C_4H_9)_4N^+$ cations and $[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]^{2-}$ anions. The methoxy groups and the squarate ligands adopt bridging coordination to the hexacoordinate Sn(IV) centers.

Introduction

The term 'oxocarbon' designates compounds in which all of the carbon atoms are bonded to carbonyl or enolic oxygens or to their hydrated or deprotonated equivalents [1, 2]. We have recently studied the chemistry of the monocyclic oxocarbon anions, squarate (**1**), croconate (**2**) and rhodizonate (**3**), with polyoxomolybdates [3–6] and have described a variety of unusual polynuclear structures. As part of these continuing investigations of the coordination chemistry of oxocarbons, the reaction of squaric acid with $SnCl_4$ in methanol was found to yield the binuclear species $[(n\text{-}C_4H_9)_4N]_2[Sn_2Cl_4(OCH_3)_2(C_4O_4))_2]$ whose structure we report in this paper.



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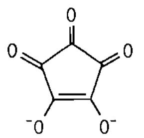

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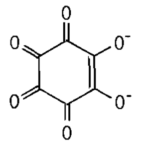

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Experimental

Preparation of $[(n\text{-}C_4H_9)_4N]_2[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]$

Tin tetrachloride and methanol were distilled prior to use. All manipulations were carried out under argon. When a solution of squaric acid (2.28 g, 20 mmol) in methanol (50 cm^3) was added to tin tetrachloride (5.21 g, 20 mmol), a vigorous exothermic reaction was observed. Upon cooling to room temperature and addition of an excess of $(n\text{-}C_4H_9)_4NCl$ and of diethyl ether, colorless crystalline blocks of the product were isolated. *Anal.* Calc. for $C_{42}H_{78}N_2O_{10}Cl_4Sn_2$: C, 43.8; H, 6.79; N, 2.44 Found: C, 43.8; H, 6.72; N, 2.32%. IR (KBr pellet, cm^{-1}): 2960(s), 2870(m), 1790(s), 1676(s), 1525(s, broad), 1425(s), 1405(s), 1072(m), 1040(m), 950(s), 879(m), 795(m), 732(s), 430(m), 348(m). The 1760 and 1676 cm^{-1} bands are associated with ν(C=O) of the coordinated squarate ligand, while the 348 cm^{-1} feature is assigned to ν(Sn–Cl).

X-ray studies

The experimental details for the X-ray structural analysis of $[(n\text{-}C_4H_9)_4N]_2[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]$ are given in Table 1. In the final refinement, all non-hydrogen atoms of the anion were refined anisotropically; the cation was treated isotropically. Idealized hydrogen atom positions were introduced assuming a bond distance of 1.09 Å for each C–H bond. The highest excursion of electron density on

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TABLE 1. Summary of experimental details for the X-ray diffraction study of $[(n\text{-}C_4H_9)_4N]_2[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]$

Crystal parameters at 296 K[a]	
a (Å)	13.914(2)
b (Å)	10.850(3)
c (Å)	19.305(4)
α (°)	90.00
β (°)	112.49(1)
γ (°)	90.0
V (Å^3)	2694.8(12)
Space group	$P2_1/c$
Z	2
D_{calc} (g cm^{-3})	1.42
Measurement of intensity data	
Crystal shape and color	colorless block
Crystal dimensions (mm)	0.32×0.29×0.34
Instrument	Nicolet R3m diffractometer
Radiation	Mo Kα (λ = 0.71073 Å)
Scan mode	coupled θ(crystal)–2θ(counter)
Scan rate (°/min)	2–30
Scan range (°)	$2.0° < 2\theta \leqslant 50°$
Scan length	from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
Background measurement	stationary crystal, stationary counter, at the beginning and at end of each 2θ scan, each for half the time taken for the scan
Standards	3 collected every 197
No. reflections collected	3529
No. reflections used in solution $F_o \geqslant 6\sigma(F_o)$	2120
Reduction of intensity data and summary of structure solution and refinement[b]: data corrected for background, attenuators, Lorentz and polarization effects in the usual fashion	
Absorption coefficient (cm^{-1})	11.7
Absorption correction (not applied)	
T_{max}/T_{min}	1.06
Structure solution	Patterson synthesis yielded the heavy atom position; all remaining non-hydrogen atoms were located via standard Fourier techniques
Atom scattering factors[c]	neutral atomic scattering factors were used throughout the analysis
Anomalous dispersion[d]	applied to all non-hydrogen atoms
Final discrepancy factor[e]	
R	0.0685
R_w	0.0697
Goodness of fit[f]	1.86

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Micro-Vax II computer using local versions of the Nicolet SHELXTL interactive crystallographic software package, as described in ref. 7. [c] Ref. 8. [d] Ref. 9. [e] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$; $R_w = [\Sigma w|F_o| - |F_c)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o + g^*(F_o))$; $g = 0.001$. [f] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

the final Fourier was 0.22 e$^-$/Å^3. Some disorder of the cation is suggested by a number of large temperature factors and a range of C–C distances. Since the final Fourier did not reveal any exceptional peaks in regions consistent with carbon locations, no further modelling of the disorder was pursued. Atomic positional coordinates are listed in Table 2.

Results and discussion

Tin(IV) is known to form a number of neutral dimeric structures of high stability and general formula $[SnCl_3LL']_2$ [8]. Tin tetrachloride will, for example, react with alcohols to yield compounds of dimeric structure $[SnCl_3(OR)(ROH)]_2$ [9]. In contrast, $SnCl_4$ was found to react readily with squaric acid in methanol to yield an anionic binuclear species, $[SnCl_2(OCH_3)(C_4O_4)]_2{}^{2-}$, isolated as the tetra-n-butylammonium salt.

The structure consists of discrete $(n\text{-}C_4H_9)_4N^+$ cations and $[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]^{2-}$ anions, whose structure is illustrated in Fig. 1. The anion possesses a center of symmetry at the midpoint of the Sn(1)–Sn(1a) vector, which relates the equivalent halves of the binuclear species. The Sn(IV) centers

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U (eq)[a]
Sn(1)	4977(1)	5143(1)	5872(1)	55(1)
Cl(1)	4498(3)	3741(4)	6611(2)	92(2)
Cl(2)	5403(3)	6807(4)	6703(2)	100(2)
O(1)	4642(6)	3944(8)	4961(4)	56(4)
O(2)	3538(6)	5502(9)	3679(5)	70(4)
O(3)	1119(7)	5955(9)	2974(5)	78(5)
O(4)	1061(7)	6145(11)	4655(5)	95(5)
O(5)	3478(6)	5761(9)	5389(5)	64(4)
C(1)	3946(12)	2975(14)	4805(9)	97(9)
C(2)	2870(9)	5691(11)	3971(7)	52(6)
C(3)	1734(9)	5885(11)	3605(8)	52(6)
C(4)	1726(9)	5996(12)	4388(8)	60(6)
C(5)	2842(9)	5788(12)	4695(9)	60(7)
N(1)	1846(7)	6233(9)	6855(5)	55(4)
C(11)	1830(10)	4958(12)	6527(8)	67(4)
C(12)	8627(11)	−1076(12)	8079(8)	75(4)
C(13)	8639(13)	−2253(14)	8489(9)	100(5)
C(14)	9018(16)	−3262(18)	8132(11)	111(7)
C(15)	2429(10)	6248(12)	7706(7)	67(4)
C(16)	3540(10)	5739(13)	7978(8)	76(4)
C(17)	4039(16)	5814(22)	8797(12)	112(7)
C(18)	3677(19)	5809(23)	9288(13)	135(9)
C(19)	2384(10)	7028(11)	6474(7)	64(4)
C(20)	2526(12)	8349(14)	6692(9)	91(5)
C(21)	2901(16)	9076(17)	6133(11)	130(7)
C(22)	3060(24)	10262(23)	6196(17)	127(11)
C(23)	755(9)	6707(7)	6725(7)	59(3)
C(24)	50(11)	6861(8)	5893(8)	81(4)
C(25)	−999(12)	7379(9)	5838(9)	97(5)
C(26)	−986(15)	8567(11)	6058(11)	107(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

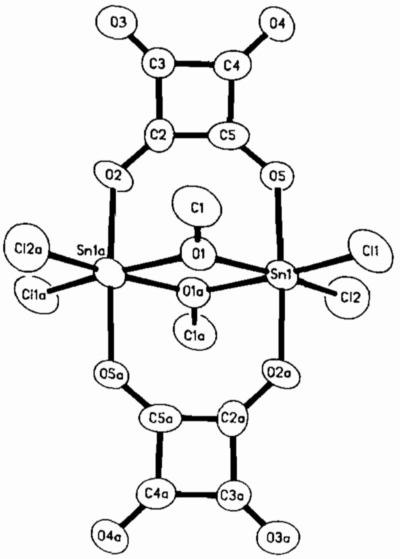


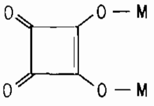
Fig. 1. ORTEP view of the structure of $[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]^{2-}$.

TABLE 3. Selected bond distances (Å) and angles (°) for $[(n\text{-}C_4H_9)_4N]_2[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]$

Sn(1)–Cl(1)	2.351(5)	O(1)–C(1)	1.38(2)
Sn(1)–C(2)	2.337(5)	O(2)–C(2)	1.27(2)
Sn(1)–O(1)	2.092(8)	O(3)–C(3)	1.19(1)
Sn(1)–O(1a)	2.120(9)	O(4)–C(4)	1.23(2)
Sn(1)–O(5)	2.045(8)	O(5)–C(5)	1.29(1)
Sn(1)–O(2a)	2.036(8)	C(2)–C(3)	1.48(2)
		C(3)–C(4)	1.52(2)
		C(4)–C(5)	1.45(2)
		C(2)–C(5)	1.42(2)

are ligated to two terminal chloride groups, the oxygen donors of two bridging methoxy groups, and two oxygen donors from the squarate ligands, which have adopted the common 1,2 bridging mode 10–14.

As shown in Table 3, the metrical parameters for the Sn coordination sphere are unexceptional. The bond distances for the squarate ligand are consistent with the formalism **4**, commonly observed for the 1,2 bridging structure, rather than the delocalized pseudoaromatic squarate form **5**. The structure is similar to that observed for $[(n\text{-}C_4H_9)_4N]_2[Mo_2(NNC_6H_5)_4(OCH_3)_2(C_4O_4)_2]$, which displays the common geometric features of bridging methoxy groups and 1,2 bridging squarate units, with the terminal chloride donors of $[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]^{2-}$ replaced by the singly bent diazenido ligands [5].



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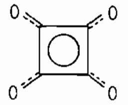

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Although the squarate ligand may assume a number of bridging geometries, the 1,2 bridging mode remains the most commonly observed. The ligand appears to be effective in the isolation of a variety of binuclear and polynuclear metal complexes, but the scope of its coordination chemistry remains largely undeveloped.

Supplementary material

Tables of bond lengths and angles, anisotropic temperature factors, calculated hydrogen atom positions and structure factors can be obtained upon request from J.Z.

Acknowledgement

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