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**Stabilization of the binuclear organotin(IV) cation  
 $[(\mu\text{-OH})(\text{Me}_3\text{Sn})_2]^+$  within the planar,  
 heterobimetallic macrocyclic anion:  
 $\{[(\mu\text{-OH})(\text{Me}_3\text{Sn})_2]_2\{(\mu\text{-NC})_2\text{Ni}(\text{CN})_2\}_2\}^{2-}$**

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**Abstract**

Reaction of  $\text{Me}_3\text{SnCl}$ ,  $\text{K}_2[\text{Ni}(\text{CN})_4]$  and  $(^n\text{Bu}_4\text{N})\text{CN}$  (2:1:1) in aqueous solution affords well-crystallizing  $[^n\text{Bu}_4\text{N}]_2\{[(\mu\text{-OH})(\text{Me}_3\text{Sn})_2]_2\{(\mu\text{-NC})_2\text{Ni}(\text{CN})_2\}_2\}$  (**2**) rather than polymeric  $[(^n\text{Bu}_4\text{N})_2(\text{Me}_3\text{Sn})_2\text{Ni}(\text{CN})_5]_\infty$ . The anion of **2** has a centrosymmetric, almost planar, 16-membered ring structure containing two non-linear  $\{(\mu\text{-OH})(\text{Me}_3\text{Sn})_2\}^+$  units with pentacoordinate Sn atoms.

In aqueous solution,  $\text{Me}_3\text{SnCl}$  is known to react instantaneously with  $\text{K}_2[\text{M}(\text{CN})_4]$  ( $\text{M} = \text{Ni}$  [1], Pd, Pt [2]) to give the polymeric species  $\{(\text{Me}_3\text{Sn}^{\text{IV}})_2\text{M}^{\text{II}}(\text{CN})_4\}_\infty$  (**1a–1c**), which probably form two-dimensional sheets involving an essentially planar  $\text{M}_n\text{Sn}_{2n}$ -skeleton [2,3]. Since spontaneous precipitation of **1**, and likewise of related 3D-polymers containing  $\text{M}(\text{CN})_6$ -units [4], is usually inhibited in the presence of Lewis bases, well-shaped faintly yellow crystals of a new product, **2**, were found to separate from solutions of  $\text{Me}_3\text{SnCl}$ ,  $\text{K}_2[\text{Ni}(\text{CN})_4]$  and  $(^n\text{Bu}_4\text{N})\text{CN}$  (2:1:1;  $\text{pH} \cong 6.2$ ) during ca. three days.

Initially, the elemental analysis suggested the composition:  $[^n\text{Bu}_4\text{N}][(\text{Me}_3\text{Sn})_2\text{Ni}(\text{CN})_5]$ , and the IR and Raman spectra in the  $\nu(\text{CN})$  absorption range were consistent with the presence of only weakly distorted square-planar or octahedral  $\text{Ni}(\text{CN})_n$  units ( $n = \text{either } 4 \text{ or } 6$ ) and trigonal bipyramidal  $\text{Me}_3\text{Sn}(\text{NC})_2$  bridges (Table 1). However, the diamagnetism of **2** is not consistent with the octahedrally coordinated  $\text{Ni}^{\text{II}}$  ions that would result if the metal ions of parallel, uniformly-stacked layers of **1a** were completely interlinked by the additional, perpendicular-oriented  $\text{CN}^-$  ions.

The result of a single-crystal X-ray study of **2** confirmed that the interpretation of the vibrational spectra and of the elemental analysis alone could have been

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Table 1

Selected infrared (IR) and Raman (Ra) bands ( $\text{cm}^{-1}$ ) for  $\text{K}_2[\text{Ni}(\text{CN})_4]$ , **1a** and **2**

Compound	$\nu(\text{CN})$		$\nu(\text{SnC})$		$\nu(\text{NiC})$
	IR	Ra	IR	Ra	IR
$\text{K}_2[\text{Ni}(\text{CN})_4]$	2127s	2151s 2127w	–	–	412s
$[(\text{Me}_3\text{Sn})_2\text{Ni}(\text{CN})_4]_\infty$ ( <b>1a</b> )	2150s	2180s 2170m	553s	556m 520s	430s
$[\text{}^n\text{Bu}_4\text{N}]_2\{(\mu\text{-OH})(\text{Me}_3\text{Sn})_2\}_2\{(\mu\text{-NC})_2\text{Ni}(\text{CN})_2\}_2\}^{2-}$ ( <b>2</b> )	2131s	2178s 2167m	550s	555m 522s	416s

misleading, since the compound turned out to involve, in addition to two  ${}^n\text{Bu}_4\text{N}^+$  cations, the novel macrocyclic dianion:  $\{[(\mu\text{-OH})(\text{Me}_3\text{Sn})_2]_2\{(\mu\text{-NC})_2\text{Ni}(\text{CN})_2\}_2\}^{2-}$  (Fig. 1). Apparently, the binuclear  $\{[(\mu\text{-OH})(\text{Me}_3\text{Sn})_2]\}^+$  cation which can be present in an aqueous solution of  $\text{Me}_3\text{SnCl}$  only as an intermediate [5], reacts very efficiently with  $[\text{Ni}(\text{CN})_4]^{2-}$  to give a sparingly soluble product. Interestingly,  $\text{Ph}_3\text{SnCl}$  has previously been shown to react with the  $[\text{Fe}(\text{CN})_6]^{4-}$  anion in dmsO to give the similarly non-polymeric product:  $[\text{PPN}]_2\{(\text{Ph}_3\text{Sn}^{\text{IV}}\text{Cl})_2(\mu\text{-NC})_2\text{-Fe}^{\text{II}}(\text{CN})_2(\text{dmsO})_2\}$  (**3**) rather than polymeric  $[(\text{Ph}_3\text{Sn}^{\text{IV}})_4\text{Fe}^{\text{II}}(\text{CN})_6]_\infty$  [6] in the presence of the larger counter-cation  $[\text{PPN}]^+$  (instead of  $\text{K}^+$ ) [7].

Table 1 presents a selection of interatomic distances and bond angles in the almost planar, centrosymmetric anion of **2**. The structure of the 16-membered ring displays several interesting features: (a) The Sn–O bond lengths are only moderately longer than the “single bond value” of ca. 2.10 Å [8]; although no hydrogen atoms could be located on the oxygen atoms, the observed Sn–O distances leave no doubt that the cyclic dianion contains two OH groups. (b) The Sn–N distances in **2** are the longest ones so far observed between a cyanide N atom and a  $\text{R}_3\text{Sn}^{\text{IV}}$  group. Interestingly, even the longest Sn–N distance in the trigonal bipyramidal  $[\text{Ph}_3\text{Sn}(\text{NCMe})_2]^+$  cation (2.472 Å [9]; Sn–N in **3**: 2.340 Å [7]) is still shorter than the shortest Sn–N distance in **2**. (c) The C(Me)–Sn–O angles are notably larger than 90°, indicating considerable distortion of the trigonal bipyramidal  $\text{Me}_3\text{Sn}(\text{NC..})(\text{OH..})$  units. Some polymers involving  $\text{Me}_3\text{Sn}(\text{OH..})(\text{NC..})$  units with inversely oriented methyl groups involving particularly long Sn–O distances have most recently been described [10].

The exceedingly long Sn–N distances in **2** are likely to account for the similarity of the  $\nu(\text{NC})$  absorption spectra of **2** and the highly symmetrical free  $[\text{Ni}(\text{CN})_4]^{2-}$  anion, justifying the view that the previously unisolated  $\{[(\mu\text{-OH})(\text{Me}_3\text{Sn})_2]\}^+$  cation is efficiently trapped in the cyclic anion of **2**. The possible use of **2** as a potential transfer reagent for the  $\{[(\mu\text{-OH})(\text{Me}_3\text{Sn})_2]\}^+$  ion (e.g. to other  $[\text{M}(\text{CN})_n]^{m-}$  anions) merits study.

## Experimental

A solution of 0.238 g (0.1 mol) of  $\text{K}_2[\text{Ni}(\text{CN})_4]$  in 25 ml of  $\text{H}_2\text{O}$  was added slowly at ca. 15°C to the clear solution of 0.60 g (0.01 mol) of  $\text{Me}_3\text{SnCl}$  and of 0.29 g (0.1 mol) of  $({}^n\text{Bu}_4\text{N})\text{CN}$  in 50 ml of  $\text{H}_2\text{O}$ . After three days ca. 0.3 g (10.1% based

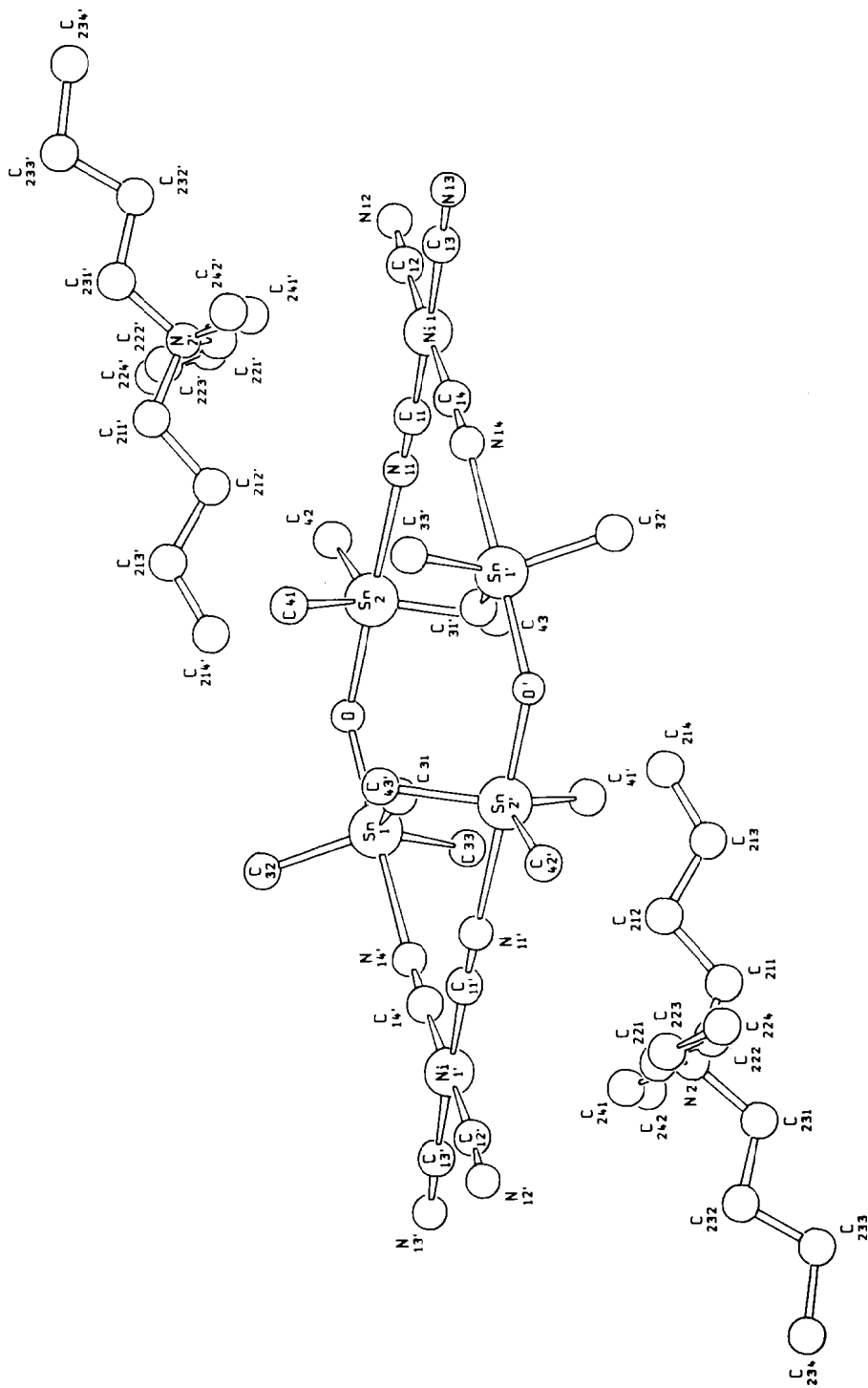


Fig. 1. SCHAKAL [12] plot of **2** with atomic numbering scheme.

Table 2

Selected interatomic distances (Å) and bond angles (°) in the anion of **2**, with esd's in parentheses.

Sn2-N11	2.529(6)	Sn1-O-Sn2	134.6(2)
Sn1-O	2.149(4)	O-Sn2-N11	174.4(1)
Sn1-C31	2.133(7)	C11-N11-Sn2	168.1(6)
Sn1-C32	2.10(1)	C31-Sn1-O	94.4(2)
Sn1-C33	2.10(1)	C32-Sn1-O	94.9(3)
Sn2-C41	2.11(1)	C33-Sn1-O	94.5(3)
Sn2-C42	2.105(7)	C41-Sn2-O	93.0(3)
Sn2-C43	2.09(1)	C42-Sn2-O	96.1(2)
Ni1-C11	1.872(6)	C43-Sn2-O	94.8(3)
Ni1-C12	1.850(7)		
Ni1-C13	1.870(6)		
Ni1-C14	1.864(7)		

on  $\text{Me}_3\text{SnCl}$  taken) of faintly yellow crystals of **2** were obtained. Elemental analysis. Found: C, 41.60; H, 7.55; N, 9.35.  $[\text{}^n\text{Bu}_4\text{N}]_2[\{(\text{OH})(\text{Me}_3\text{Sn})_2\}_2\{\text{Ni}(\text{CN})_4\}_2]/[\text{}^n\text{Bu}_4\text{N}][(\text{Me}_3\text{Sn})_2\text{Ni}(\text{CN})_5]$  calc.: C, 40.72/41.04; H, 7.36/7.15; N, 9.13/12.89%. **2** is significantly water-soluble above ca. 15°C, and decomposes thermally above 122°C.

Structural data for **2** [11\*]: Syntex  $P2_1$  four-circle diffractometer, graphite monochromator ( $\text{Mo-K}_\alpha$  radiation,  $\lambda$  0.71069 Å). Temperature 293 K, crystal dimensions 0.65 × 1.12 × 0.52 mm,  $M_r$  1499.76. Monoclinic,  $P2_1/c$  (No. 14);  $a$  8.920(2),  $b$  18.964(4),  $c$  22.457(5) Å;  $\beta$  99.83(1)°;  $U$  3743.1(1) Å<sup>3</sup>.  $Z = 2$ .  $D_x$  1.331 g cm<sup>-3</sup>;  $2\theta$  range: 4.5–55°,  $\mu$  18.5 cm<sup>-1</sup>;  $F(000)$  1528. Measured reflections: 9423, symmetry-independent reflections: 7786, number of observed reflections with  $F_o > 6\sigma(F_o)$ : 5259. Refinement of 312 parameters. Three-dimensional Patterson synthesis, refinement of all non-hydrogen atoms (except C244) by least squares; fixation of the distances C242–C243 and C243–C244 to  $1.53 \pm 0.05$  Å; H-atoms on C244 were not included owing to disorder of C244. Final  $R$  values:  $R = 0.0535$ ,  $R_w = 0.0631$  with  $w = [\sigma^2(F_o) + 0.0003 \cdot F_o^2]^{-1}$ .

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