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Crystal Engineering with Oxo- and Cyanocarbon Anions: Synthesis and Structural Characterization of Triorganotin(IV) Pentacyanopropenides and Hexacyanoazapentadienides

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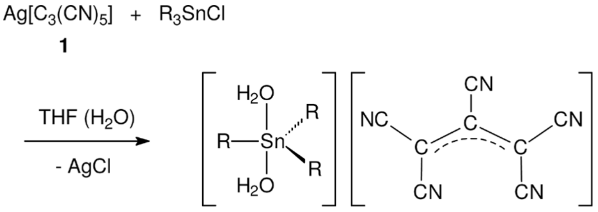
Abstract. The first triorganotin(IV) pentacyanopropenides, $[R_3Sn(H_2O)_2][C_3(CN)_5]$ (R = Me (**2**), *n*Bu (**3**), Ph (**4**) were prepared by treatment of $Ag[C_3(CN)_5]$ (**1**) with equimolar amounts of R_3SnCl in reagent grade THF. In a similar manner, dark red $[R_3Sn(H_2O)_2][N\{C(CN)C(CN)_2\}_2]$ (**6**) containing the hexacyanoazapentadienyl anion was prepared in 55 % yield. The molecular structure of $[Ph_3Sn(H_2O)_2][C_3(CN)_5]$ (**4**) was determined by X-ray diffraction. The crystal structure consists of separated trigonal-bipyramidal $[Ph_3Sn(H_2O)_2]^+$ cations and nearly planar $[C_3(CN)_5]^-$ anions which are linked through O–H···N hydrogen bonds to give a three-dimensional network.

Introduction

Triorganotin compounds are of current interest for various reasons. Among the commercial applications is the extensive use of tributyltin derivatives (e.g. halides, oxides, and acetates) as wood preservatives and marine antifouling paints. However, these uses have caused considerable environmental concerns in recent years.[1] Triphenyltin derivatives such as triphenyltin acetate are commercially used as agricultural fungicides.[2] Many other organotin derivatives are currently being investigated due to their promising antitumor properties.[3] In most cases it was found that triorganotin compounds display a higher biomedical activity than their mono- or diorganotin counterparts.[4] Last, but not least, it is well established that numerous organotin derivatives have a highly diverse structural chemistry and give rise to a variety of supramolecular structures.[5] Thus, these species are excellent targets for studies in the area of crystal engineering. It was the latter aspect that prompted us to investigate the preparation and structural characterization of a series of triorganotin pentacyanopropenides. The pentacyanopropenide anion, $[C_3(CN)_5]^-$, belongs to a series of cyanocarbon anions comprising a plurality of cyano groups juxtaposed in such a way that they cannot all coordinate to the same metal atom. Typically, the entire cyanocarbon skeleton is almost planar, allowing for extensive electronic delocalization. The discovery of these fascinating materials dates back to the pioneering work of *Middleton* and *Webster* et al. at DuPont.[6] Although they are frequently found as unbound counterions or monodentate ligands, they often act as bridging ligands affording polymeric coordination compounds.[7] Like the oxocarbon anions $C_nO_n^{2-}$,[8] the cyanocarbon anions are ideal multiform building blocks for crystal engineering.[9] We report here the synthesis and structural characterization of the first triorganotin(IV) derivatives of cyanocarbon anions.

Results and Discussion

As a logical synthetic pathway to triorganotin(IV) pentacyanopropenides the reaction of triorganotin halides with the readily available silver pentacyanopropenide, $Ag[C_3(CN)_5]$ (**1**),[6b,10] was chosen. These reactions were carried out in suitable solvents such as THF, dichloromethane or acetonitrile. It soon became clear that under strictly anhydrous conditions the heterogeneous reactions were very sluggish and incomplete. Even after prolonged reaction times no well-defined crystalline reaction



2: R = Me
3: R = ^{n}Bu
4: R = Ph

Scheme 1. Synthesis of the triorganotin(IV) pentacyanopropenides **2**–**4**.

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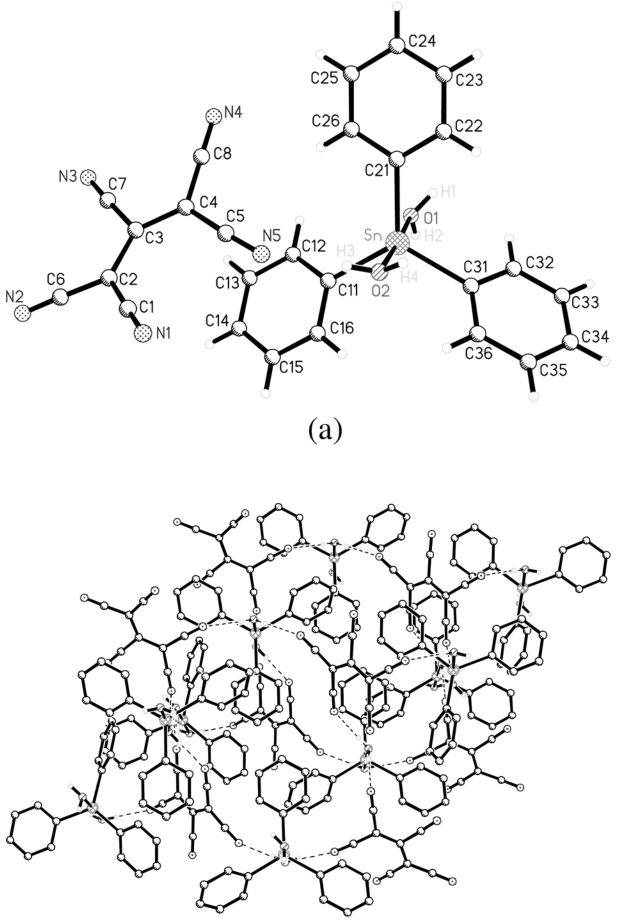
products could be isolated. However, it was found that the conversions were greatly accelerated by the presence of small amounts of water, i.e. when the solvents were not specially dried and used as received. The best results were obtained in THF as reaction medium. X-ray structure analyses carried out on the products (vide infra) revealed, that this leads to the formation of $[R_3Sn(H_2O)_2]^+$ cations. Thus, the overall reactions can be formulated as illustrated in Scheme 1.

All three new compounds **2**–**4** were isolated in the form of light yellow crystals, which are readily soluble in polar organic solvents such as THF, diethyl ether, and dichloromethane, but virtually insoluble in hydrocarbon solvents. The compounds were characterized by elemental analyses as well as the usual spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR). The IR spectra display a very strong band slightly above 2200 cm^{-1}, which can be readily assigned to the ν(C≡N) vibration. It has been noted earlier that these bands are not significantly influenced by the coordination mode of the pentacyanopropenide ion and differ only in their intensity ratios.[7a] The same effect was found for the bands of the ν(C=C) vibrations. As expected, the ^{13}C NMR spectra display three signals for the CN groups which are found in the narrow range of 112.9–117.2 ppm. The resonances of the carbon atoms of the propenide unit are observed at ca. 136 ppm (central carbon atom C-3) and ca. 57 ppm (outer carbon atoms C-2,4) (cf. Figure 1a). These values are in excellent agreement with those reported in the literature.[7]



(a)

(b)

Figure 1. Molecular (a) and crystal (b) structure of $[Ph_3Sn(H_2O)_2][C_3(CN)_5]$ (**4**).

The molecular structure of **4** was determined by X-ray diffraction (Figure 1, Table 1). The crystal structure comprises separated $[Ph_3Sn(H_2O)_2]^+$ cations and nearly planar pentacyanopropenide anions. The coordination geometry around tin in the $[Ph_3Sn(H_2O)_2]^+$ cation[11] is nearly perfect trigonal-bipyramidal with the phenyl substituents occupying the equatorial positions (O1–Sn–O2: 177.85(5)°). With 212.19(17), 212.50(16), and 212.52(17) pm, the three Sn–C bond lengths are virtually identical (Table 2).

Table 1. Crystallographic Data for $[Ph_3Sn(H_2O)_2][C_3(CN)_5]$ (**4**).

	4
Identification code	15_00md
Empirical formula	$C_{26}H_{19}N_5O_2Sn$
Formula weight	552.18
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.2537(1) Å, α = 90°
	b = 20.9291(3) Å, β = 103.843(1)°
	c = 14.8407(1) Å, γ = 90°
Volume	5387.1(3) Å^3
Z	4
Density (calculated)	1.251 Mg·m^{-3}
Absorption coefficient	1.058 mm^{-1}
F(000)	1104
Crystal size	0.6 × 0.6 × 0.4 mm
Theta range for data collection	1.72 to 28.00°
Reflections collected	16185
Index ranges	$-10 \leq h \leq 10$
	$-27 \leq k \leq 21$
	$-19 \leq l \leq 19$
Independent reflections	5969 [R(int) = 0.0267]
Completeness to θ = 29.23°	99.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Max./ min. transmission	0.6769 and 0.5693
Data / restraints / parameters	5969 / 6 / 325
Goodness-of-fit on F^2	1.017
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0239, $wR2$ = 0.0573
R indices (all data)	$R1$ = 0.0291, $wR2$ = 0.0594
Extinction coefficient	0.0071(3)
Largest diff. peak and hole	1.041 and –0.805 e·Å^{-3}

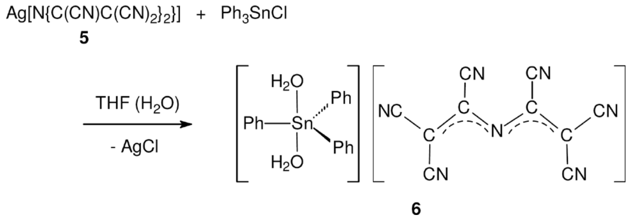
The structural parameters within the $[C_3(CN)_5]^-$ anion closely resemble those reported in the literature for other pentacyanopropenide salts and coordination compounds.[7,12] With C–C bond lengths of 140.0(2) Å (C2–C3) and 139.7(2) pm (C3–C4) the central allylic unit clearly shows evidence for multiple bonding between the three carbon atoms with an almost ideal symmetrical electronic delocalization. The C–CN distances amount to 145.6(2) pm (C3–C7) for the central carbon atom and are slightly shorter for the outer carbon atoms (142.2(2) to 142.8(2) pm). These values are favorably similar to those reported earlier, e.g. for $[Et_4N][W(CO)_5\{C_3(CN)_5\}]$.[12f] The

Table 2. Selected bond lengths /pm and angles /° for $[Ph_3Sn(H_2O)_2]$-$[C_3(CN)_5]$ (**4**).

Sn–C(11)	212.19(17)
Sn–C(31)	212.50(16)
Sn–C(21)	212.52(17)
Sn–O(2)	227.21(13)
Sn–O(1)	231.82(13)
C(1)–N(1)	114.2(2)
C(1)–C(2)	142.6(2)
C(2)–C(3)	140.0(2)
C(2)–C(6)	142.8(2)
C(3)–C(4)	139.7(2)
C(3)–C(7)	145.6(2)
C(4)–C(8)	142.2(2)
C(4)–C(5)	142.5(2)
C(5)–N(5)	115.0(2)
C(6)–N(2)	114.5(2)
C(7)–N(3)	113.9(2)
C(8)–N(4)	115.3(3)
C(31)–Sn–O(2)	88.25(6)
C(21)–Sn–O(2)	95.72(6)
C(11)–Sn–O(1)	89.67(6)
C(31)–Sn–O(1)	93.87(6)
C(21)–Sn–O(1)	83.55(6)
O(2)–Sn–O(1)	177.85(5)
C(11)–Sn–C(31)	120.36(7)
C(11)–Sn–C(21)	120.21(7)
C(31)–Sn–C(21)	119.34(7)
C(11)–Sn–O(2)	88.96(5)
N(1)–C(1)–C(2)	177.3(2)
C(3)–C(2)–C(1)	121.24(15)
C(3)–C(2)–C(6)	121.36(15)
C(1)–C(2)–C(6)	117.25(15)
C(4)–C(3)–C(2)	128.81(15)
C(4)–C(3)–C(7)	115.17(14)
C(2)–C(3)–C(7)	116.00(14)
C(3)–C(4)–C(8)	119.56(15)
C(3)–C(4)–C(5)	124.48(15)
C(8)–C(4)–C(5)	115.91(16)
N(5)–C(5)–C(4)	176.7(2)
N(2)–C(6)–C(2)	178.6(2)
N(3)–C(7)–C(3)	178.21(19)
N(4)–C(8)–C(4)	179.2(2)

same is true for the C–N bond lengths (113.9(2) to 115.3(3) pm). In the crystal structure (Figure 1b), the two ionic moieties are connected through O–H···N hydrogen bonds. Each hydrogen atom of the coordinated water molecules $[Ph_3Sn(H_2O)_2]^+$ cation interacts in this way with a cyano group of the $[C_3(CN)_5]^-$ anion to give a three-dimensional network in the solid state.

In a similar manner, the hitherto unknown $[Ph_3Sn(H_2O)_2]^+$-salt of the more extended hexacyanoazapentadienyl anion $[N\{C(CN)C(CN)_2\}_2]^-$[6b] was prepared according to Scheme 2. Treatment of the readily accessible silver salt $Ag[N\{C(CN)C(CN)_2\}_2]$,[6b,13] suspended in reagent grade THF, with an equimolar amount of Ph_3SnCl afforded the dark red hydrated triphenyltin(IV) derivative $[Ph_3Sn(H_2O)_2]$ $[N\{C(CN)C(CN)_2\}_2]$ (**6**) in 55 % yield. Compound **6** was characterized by elemental analysis as well as by IR and NMR spectroscopy, but failed to produce X-ray quality single-crystals despite several attempts using different solvent mixtures for recrystallization. The IR spectrum showed a very strong band at 2205 cm^{-1}, which could be readily assigned to the ν(C≡N) vibration.



Scheme 2. Synthesis of $[Ph_3Sn(H_2O)_2][N\{C(CN)C(CN)_2\}_2]$ (**6**).

Conclusions

The first triorganotin(IV) derivatives of cyanocarbon anions were synthesized and characterized. Surprisingly, the reactions according to Scheme 1 and Scheme 2 worked well only in the presence of minor amounts of water to give the salt-like species $[R_3Sn(H_2O)_2][C_3(CN)_5]$ (R = Me (**2**), *n*Bu (**3**), Ph (**4**) and $[R_3Sn(H_2O)_2]$ $[N\{C(CN)C(CN)_2\}_2]$ (**6**) in moderate to good yields. The molecular and crystal structure of $[Ph_3Sn(H_2O)_2][C_3(CN)_5]$ (**4**) was determined by X-ray diffraction. The crystal structure consists of separated trigonal-bipyramidal $[Ph_3Sn(H_2O)_2]^+$ cations and nearly planar $[C_3(CN)_5]^-$ anions which are linked through O–H···N hydrogen bonds to give a three-dimensional network.

Experimental Section

The reactions were carried out under ambient conditions without any special precautions to exclude air or moisture. Reagent grade THF was used as received without drying. IR spectra were recorded with a Perkin–Elmer FT-IR spectrometer System 2000. NMR spectra were recorded in DMSO-d_6 with a Bruker DPX 400 NMR spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz). Microanalyses were performed at the Chemistry Department, Otto-von-Guericke-Universität Magdeburg. The starting materials $Ag[C_3(CN)_5]$ (**1**)[6b] and $Ag[N\{C(CN)C(CN)_2\}_2]$ (**5**)[13] were prepared according to the literature procedure whereas the triorganotin halides R_3SnCl (R = Me, *n*Bu, Ph) were commercially available (Aldrich). The Mass spectrum (EI, 70 eV) was measured with a MAT 95 apparatus. Microanalysis was performed using a Leco CHNS 923 or a VARIO EL cube apparatus. The intensity data of **4** were collected using a Stoe IPDS 2T diffractometer with Mo-K_α radiation. The data were collected with the Stoe XAREA[14] program using ω-scans. Space groups were determined with XRED32[14] program. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 using SHELXL-97.[15]

Preparation of Compounds 2–4 (General Procedure)

To a suspension of $Ag[C_3(CN)_5]$ (**1**, 0.55 g, 2 mmol) in reagent grade THF (20 mL) was added a solution of R_3SnCl (2 mmol, R = Me: 0.40 g; R = *n*Bu: 0.65 g; R = Ph: 0.77 g) in THF (20 mL) and the mixture was stirred at room temp. for 24 h. AgCl was removed by filtration and the clear filtrate was concentrated in vacuo to a total volume of ca. 20 mL. The resulting yellow solution was carefully layered with n-pentane and left to stand undisturbed for a few days to give pale yellow crystals of the product. Further purification could be achieved by recrystallization from diethyl ether.

[$Me_3Sn(H_2O)_2$][$C_3(CN)_5$] (2): Yield: 0.53 g (72 %), m.p. 121 °C. $C_{11}H_{13}N_5O_2Sn$ (365.97): C 36.10, H 3.58, N 19.14; found: C 36.23, H 3.73, N 19.60 %. **IR** (KBr): $\tilde{\nu}$ = 2997 (m), 2206 (vs, C≡N)), 1507 (vs, C=C), 1487 (m), 1386 (m), 794 (m), 557 (s) cm^{-1}. **^{1}H NMR** (400.13 MHz, [D_6]DMSO, 25 °C): δ = 0.54 (s, 9 H, CH_3). **^{13}C NMR** (100.62 MHz, [D_6]DMSO, 25 °C): δ = 135.7 (C-3); 117.2, 113.9, 113.3 (*C*≡N); 57.0 (C-2,4); 0.68 (CH_3).

[*n*$Bu_3Sn(H_2O)_2$][$C_3(CN)_5$] (3): Yield: 0.50 g (51 %), m.p. 112 °C. $C_{20}H_{31}N_5O_2Sn$ (492.21): C 48.80, H 6.35, N 14.23; found: C 48.28, H 5.95, N 14.11 %. **IR** (KBr): $\tilde{\nu}$ = 2208 (vs, C≡N), 1548 (vs), 1506 (vs, C=C), 1484 (m), 1417 (m), 1378 (m), 1259 (m), 535 (s) cm^{-1}. **^{1}H NMR** (400.13 MHz, [D_6]DMSO, 25 °C): δ = 1.22 (m, 6 H, CH_2), 1.29 (m, 6 H, CH_2), 0.93 (m, 6 H, CH_2), 0.06 (s, 9 H, CH_3). **^{13}C NMR** (100.62 MHz, [D_6]DMSO, 25 °C): δ = 135.1 (C-3); 116.0, 114.3, 113.1 (*C*≡N); 57.2 (C-2,4); 27.9, 26.8, 17.8 (*C*H_2); 13.6 (*C*H_3).

[$Ph_3Sn(H_2O)_2$][$C_3(CN)_5$] (4): Yield: 0.83 g (75 %), m.p. 127 °C. $C_{26}H_{19}N_5O_2Sn$ (552.18): C 56.56, H 3.47, N 12.68; found: C 55.65, H 3.38, N 12.82 %. **IR** (KBr): $\tilde{\nu}$ = 3068 (m), 2208 (vs, C≡N), 1578 (m), 1503 (vs, C=C), 1430 (s), 1385 (m), 1195 (m), 1076 (m), 997 (w), 731 (s), 669 (s) cm^{-1}. **^{1}H NMR** (400.13 MHz, [D_6]DMSO, 25 °C): δ = 7.81, 7.79, 7.55 (m, Ph). **^{13}C NMR** (100.62 MHz, [D_6]DMSO, 25 °C): δ = 135.9 (C-3); 134.0, 133.1, 130.2, 129.2 (Ph); 116.4, 114.0, 112.9 (*C*≡N); 57.1 (C-2,4).

Preparation of [$Ph_3Sn(H_2O)_2$][N{C(CN)C(CN)$_2$}$_2$] (6)

Solid Ph_3SnCl (0.39 g, 1.0 mmol) was added in one portion to a stirred suspension of Ag[N{C(CN)C(CN)$_2$}$_2$] (**5**, 0.33 g, 1.0 mmol) in THF (20 mL) and the reaction mixture was stirred at room temp. for 24 h. After removal of the solvent in vacuo, the residue was extracted with diethyl ether (30 mL). Insoluble material was filtered off, and the filtrate was again evaporated to dryness. The crude product was redissolved in a THF/toluene mixture (1:2, 20 mL) and carefully layered with *n*-pentane to produce dark red crystals of **6** after standing undisturbed for a few days. Yield: 0.83 g (55 %), m.p. 127 °C. $C_{28}H_{19}N_7O_2Sn$ (604.21): C 55.66, H 3.17, N 16.23; found: C 54.97, H 2.95, N 15.82 %. **IR** (KBr): $\tilde{\nu}$ = 3060 (m), 2205 (vs, CN), 1588 (m), 1500 (vs, C=C), 1428 (s), 1411 (s), 1383 (m), 1188 (m), 1067 (m), 1002 (w), 735 (s), 658 (s) cm^{-1}. **^{1}H NMR** (400.13 MHz, [D_6]DMSO, 25 °C): δ = 7.48, 7.25 (m, Ph). **^{13}C NMR** (100.62 MHz, [D_6]DMSO, 25 °C): δ = 135.7 (*C*(CN)); 133.2, 130.7, 129.3, 128.8 (Ph); 57.1 (*C*(CN)$_2$).

Crystallographic data for the crystal structure reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/) by referring to the CIF deposition code CCDC-233441.

Supporting Information (see footnote on the first page of this article): ORTEP drawings and X-ray structural data as well as complete CIF file for **4**.

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