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Short Communication

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Crystal structure of the triphenyltin(IV) chloride dimethyl *N*-cyanodithioiminocarbonate adduct

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Abstract: Reaction of dimethyl *N*-cyanodithioiminocarbonate, $NCNC(SCH_3)_2$ (**L**), and $SnPh_3Cl$ led to the formation of $[ClPh_3SnNCNC(SCH_3)_2]$ (**1**) which crystallizes in the monoclinic space group *C*2/c with *Z*=8, *a*=19.152(2) Å, *b*=12.8659 (16) Å, *c*=19.063(3) Å, *β*=108.608(3) and *V*=4451.6(10) Å^3. The structure of **1** consists of a $SnPh_3$ moiety *trans*-coordinated in apical positions by one **L** ligand, *N*-coordinated, and one chlorine atom involving a trigonal bipyramid geometry around the Sn(IV) atom. To our knowledge, this is the first isolation of a discrete triorganotin(IV) complex with a *N*-cyanodithioiminocarbonate adduct. The structural characterization of **1** was completed by infrared and nuclear magnetic resonance spectroscopy, and elemental analysis which confirm the X-ray elucidation.

Keywords: coordination complex; cyanamide derivative; *N*-ligand; triphenyltin; X-ray crystallography.

In the past, there were relatively few investigations in the literature on the main group metal complexes with cyanamide adducts (N≡C-N-). Early studies on this domain date back to the 1970s (Seltzer, 1968; Jain and Rivest, 1970). More recently, organoheterobimetallic cyanodithioimidocarbonates involving tin-based complexes have been also reported for electrical conducting properties (Singh and Kumar, 2008). To the best of our knowledge and up to now, only three examples, especially of tin(IV) derivatives, have been crystallographically resolved, exhibiting essentially polymeric structures: $(CH_3)_2Sn[N(CN)_2]_2$ and $(CH_3)_3Sn[N(CN)_2]$ (Chow, 1971), and $(CH_3)_3Sn[NCNNO_2]$ (Jäger et al., 1997).

In our ongoing studies on *N*-ligands coordinated to organotin(IV) moieties (Sow et al., 2012) we focused on the reactivity of dimethyl *N*-cyanodithioiminocarbonate, $NCNC(SCH_3)_2$ (**L**), a precursor for the synthesis of quinazolinone derivatives (Al-Salahi et al., 2014), with Ph_3SnCl. The resulting complex **1** has been characterized by infrared and multinuclear nuclear magnetic resonance (NMR) spectroscopy (^1H, $^{13}C\{^1H\}$, and $^{119}Sn\{^1H\}$), and its structure was finally determined by an X-ray crystallographic analysis. While the cyanodithioimidocarbonate, $[NCNCS_2]^{2-}$, dianion commonly adopts the S,S-bidentate bridging coordination mode (Burchell et al., 2004), **L** in which both sulfur atoms are methylated was found in **1** to be a monodentate *N*-ligand (Scheme 1). To date, such a structure is rather uncommon. The only examples are described for transition metal complexes. The first one was the copper complex, $CuCl_2[NCNC(SCH_3)_2]_2$ (Kojic-Prodic et al., 1992). Recently, some of us have isolated two new specimens, reporting the crystal structure of dichloridobis(dimethyl *N*-cyanodithioiminocarbonate)cobalt(II) (Diop et al., 2016a) and then dichloridobis(dimethyl *N*-cyanodithioiminocarbonate)zinc (Diop et al., 2016b).

Compound **1** was first studied by middle and far infrared spectroscopy [attenuated total reflectance (ATR) mode], and its spectrum was compared to those of the free **L** ligand and Ph_3SnCl (Figures S1 and S2, respectively). The shift of the ν(C≡N) band to a higher frequency by 20 cm^{-1} constitutes the most notable observation which can be explained by the coordination of **L** to Sn atom through the nitrogen atom of the cyano group. Additional vibration bands, characteristic of phenyl ligands (Ph, C_6H_5), are also observed at 732 and 696 cm^{-1} corresponding to $\delta(C_{sp2}\text{-}H)$ and $\delta(C=C)$ elongations, respectively. The far infrared spectrum of **1** combines the fingerprints of Ph_3SnCl and **L** and

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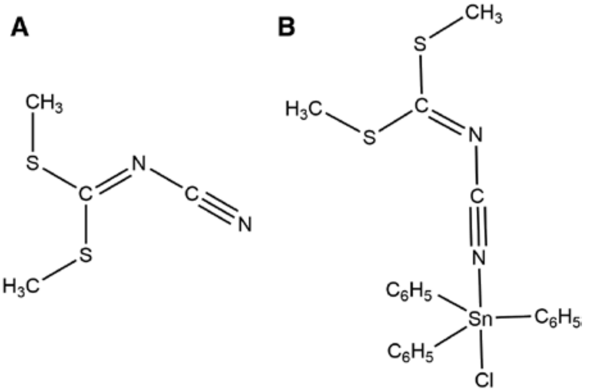

Scheme 1: Molecular representations of (A) **L** and (B) **1**.

evidences in the region of 330 cm^{-1} the absence of the ν(Sn-Cl) band (Tudela and Calleja, 1993), as already observed before for such Ph_3SnCl adducts (Sall et al., 1995). The CHNS elemental analysis performed on crystals also supports the proposed formula. Furthermore, compound **1** is well soluble in chlorinated and aromatic solvents. ^1H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$ and toluene-d8 highlight the characteristic signals of **L** and phenyl groups and confirm the 1:3 ratio (Figures S2 and S3). The $^{119}Sn\{^1H\}$ NMR spectrum in $CDCl_3$ exhibits only one resonance at -47.8 ppm ($SnMe_4$ as external reference, Figure S4) showing a very slight shift to higher field with respect to $SnPh_3Cl$ used as organotin precursor (δ=44.7 ppm in $CDCl_3$, Carcelli et al., 1992). A comparable observation was made in toluene-d8 with δ=50.9 ppm. A concentration dependence study was also investigated in CD_2Cl_2 solution at 300 K involving a limited effect on the values of $\delta(^{119}Sn\{^1H\})$ [0.5 M, δ=-49.9 ppm; 1 M, δ=-51.2 ppm; 2 M, δ=-52.1 ppm] (Figure S6). However, the spectra recorded for the 0.5 and 1 M solutions exhibit broad signals. Such $^{119}Sn\{^1H\}$ NMR chemical shift values are in line with the presence of four-coordinate species (Holeček et al., 1983). On the basis of the five-coordination of **1** (Scheme 1b), values in the range of -180 to -260 ppm would rather be expected (Holeček et al., 1983). Thus, the probable dissociation of **L** occurs in solution. Indeed, triphenyltin(IV) adducts are known to be unstable in solution releasing Ph_3SnCl. To date, several examples have been already reported in the literature (Momeni et al., 2010; Gholivand et al., 2014). Similar conclusions are also supported by middle infrared measurements (transmission mode) in solution (CH_2Cl_2). The frequency of the ν(CN) band recorded for **1** fits nearly with that of the free ligand **L** measured under the same conditions (Figure S7).

The coordination of **L** to an organotin(IV) moiety was definitively verified in the solid state by an X-ray crystallographic analysis performed on suitable crystals. Crystallographic data and refinement details are summarized in Table 1. An ORTEP view with selected bond lengths and angles (Å, °) is shown in Figure 1. The dimethyl *N*-cyanodithioiminocarbonate ligand was found disordered over two positions with occupation factors equal to 0.5, due to the steric hindrance between the two closer molecules. The structure of **1** corresponds to a $SnPh_3$ moiety *trans*-coordinated by one **L** ligand, *N*-coordinated, and one chlorine atom, terminally bonded. The environment around the tin(IV) atom can be viewed as trigonal bipyramidal (tbp). Thus, the three phenyl groups occupy the equatorial planes [Sn-C1 2.1198(17), Sn-C7 2.1345(17), and Sn-C13 2.1345(17) Å]. The sum of the angles at tin [C1-Sn-C7 121.00(6), C1-Sn-C13 114.49(6), and C13-Sn-C7 121.86(6)] is equal to 357.35°. The Sn-C distances are in the range of those found in tbp $SnPh_3$ moieties (Pelizzi and Pelizzi, 1983). The apical positions are occupied by chlorine and nitrogen atoms [Sn-Cl 2.4717(5) and Sn-N1 2.5360(14) Å]. The Cl-Sn-N angle [177.13(4)°] reveals a slight deviation from linearity. Compared to the two existing examples of chlorotriphenyltin complexes with a cyano adduct, already described in the literature (Carini et al., 1990; Carcelli et al., 1992), some structural disparities are observed with **1** and are reported in Table 2. Thus, the Sn-N distance of **1**, longer than in the two examples given, reflects the weak coordination of **L** and can explain the facile dissociation observed in solution, leading to the release of the starting tin(IV) complex.

As mentioned before, X-ray structures of triorganotin(IV) complexes with cyanamide adducts were rather rare and until now exclusively describe polymeric networks. Thus and to the best of our knowledge, the isolation of **1** in the solid state is the first example of a monomeric organotin complex bearing a terminal dimethyl *N*-cyanodithioiminocarbonate ligand. Further work is in progress with the aim to isolate such new derivatives.

Experimental

General

Dimethyl *N*-cyanodithioiminocarbonate [$NCNC(SCH_3)_2$, 90% purity] and triphenyltin chloride ($SnPh_3Cl$, 95% purity) were purchased from Sigma-Aldrich (Steinheim am Albuch, Germany) and were used without any further purification. Middle infrared spectra (4000–500 cm^{-1}) of solid samples were recorded on a Bruker Vector 22 spectrometer (Wissembourg, France) equipped with a Specac Golden Gate™ ATR device. The far FT-IR measurements (700–70 cm^{-1}) were performed by using a Bruker Vertex 70v spectrometer under vacuum (Wissembourg, France), with an ATR module. Middle infrared spectra of liquid solutions were recorded in transmission mode on a Bruker

Table 1: Crystal data and structure refinement of **1**.

Formula	$C_{22}H_{21}ClN_2S_2Sn$	
Formula weight, g/mol	531.67	
Temperature	100(2) K	
Crystal system	Monoclinic	
Space group	*C*2/*C*	
Unit cell dimensions	a=19.152(2) Å	α=90°
	b=12.8659(16) Å	β=108.608(3)°
	c=19.063(3) Å	γ=90°
Volume	4451.6(10) $Å^3$	
Z	8	
Density (calculated)	1.587 mg/m^3	
Absorption coefficient	1.466 mm^{-1}	
F(000)	2128	
Crystal size, mm	0.50×0.20×0.12	
θ range for data collection	3.235 to 57.584°	
Index ranges	$-24 \leq h \leq 24$, $-16 \leq k \leq 16$, $-24 \leq l \leq 24$	
Reflections collected	88554	
Independent reflections	5141 [*R*(int)=0.0213]	
Completeness to θ_{max}	99.7%	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5141/255/298	
Goodness-of-fit[c] on F^2	1.186	
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0205[a], wR_2=0.0411[b]	
R indices (all data)	R_1=0.0236, wR_2=0.0436	
Largest difference peak/hole, e/$Å^3$	0.791/-0.371	
CCDC number	1472446	

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w=1/[\sigma^2(F_o^2)+11.0969P+(0.0071P)^2]$ where $P=(\max(F_o^2,0)+2*F_c^2)/3$; [c] goodness of fit=$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$.

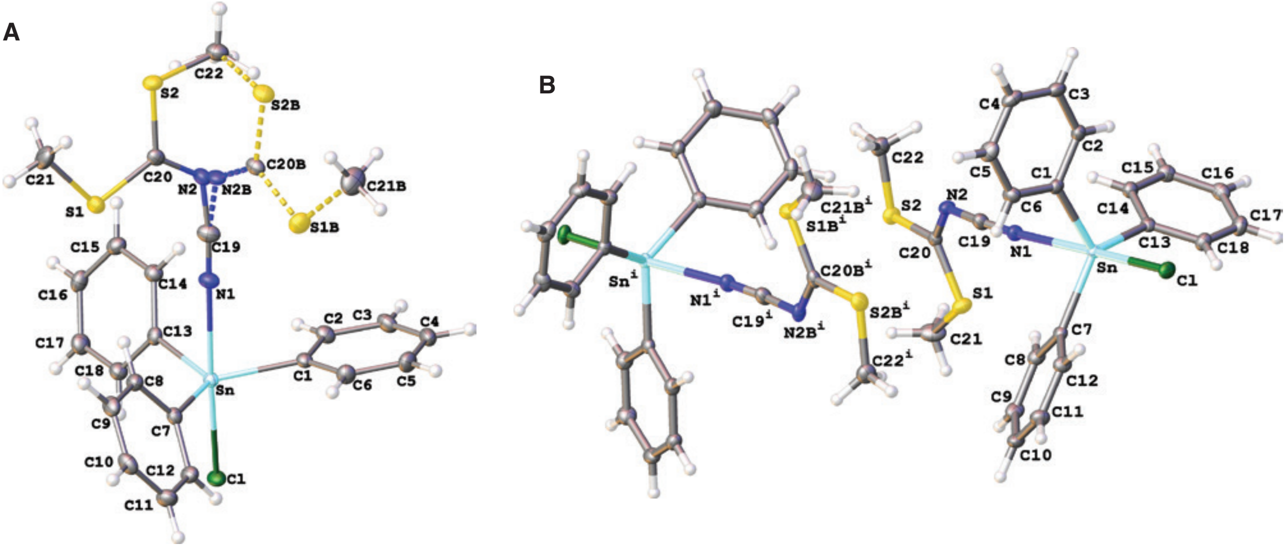

Figure 1: Molecular structure of [$ClPh_3SnNCNC(SCH_3)_2$] (**1**) showing 30% probability ellipsoids and the crystallographic numbering scheme [Ortep views. A) Showing the two positions of the dimethyl *N*-cyanodithioiminocarbonate ligand, B) showing the positioning between two molecules].
Selected bond lengths and angles (Å, °): Sn-Cl 2.4717(5), Sn-N1 2.5360(14), Sn-C1 2.1198(17), C1-Sn-Nl 83.30(5), Sn-C7 2.1345(17), Sn-C13 2.1345(17), N1-C19 1.148(2), C19-N2 1.342(14), N2-C20 1.290(13), C20-S1 1.740(3), C20-S2 1.724(3), S1-C21 1.799(10), S2-C22 1.748(2); Cl-Sn-N1 177.13(4), C1-Sn-Cl 95.03(4), C1-Sn-N1 83.30(5), C1-Sn-C7 121.00(6), C1-Sn-C13 114.49(6), C7-Sn-Cl 94.97(5), C7-Sn-N1 83.93(5), C13-Sn-Cl 96.24(5), C13-Sn-N1 86.58(6), C13-Sn-C7 121.86(6), C19-N1-Sn 175.75(14), C20-N2-C19 125.0(11), N1-C19-N2 172.0(6), N2-C20-S1 121.6(7), N2-C20-S2 120.3(7), S1-C20-S2 118.1(2). Symmetry transformation: (i) 1-x, y, 0.5-z.

Table 2: Comparison of Sn-Cl, Sn-N, and (Sn)N≡C bond lengths (Å), and Cl-Sn-N angles (°) in cyano derivatives of chlorotriphenyltin(IV) complexes.

Compounds	Sn-Cl (Å)	Sn-N (Å)	(Sn)N≡C (Å)	Cl-Sn-N (deg)	CSD Identifier
$[(ClPh_3Sn)_2(\mu\text{-}NC)_2Fe(CN)_2(dmso)_2]^-$ (Carini et al., 1990)	2.535(3)	2.340(7)	1.16(1)	175.5(2)	JEFTET
$[ClPh_3Sn(m\text{-}NC)Ag(CN)]^-$ (Carcelli et al., 1992)	2.518(23)	2.436(3)	1.138(8)	175.5(1)	JOYVEY
$[ClPh_3SnNCNC(SCH_3)_2]$ (**1**) (this work)	2.4717(5)	2.5360(14)	1.148(2)	177.13(4)	

Alpha spectrometer (Wissembourg, France). The NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer with a wideband sensor broad band fluorine observation (BBFO). ^1H and $^{13}C\{^1H\}$ chemical shifts (δ, ppm) were determined from the residual solvent signal ($C\mathit{H}Cl_3$ δ=7.26 and $\mathit{C}HCl_3$ δ=77.16). $^{119}Sn\{^1H\}$ chemical shifts (δ, ppm) were reported downfield from $(CH_3)_4Sn$ used as external standard. Elemental analyses were performed at the Institut de Chimie Moléculaire (Université de Bourgogne Franche-Comté, Dijon-France) using a Thermo Electron CHNS/O Flash EA 112 Series analyser.

Synthesis and isolation of $[ClPh_3SnNCNC(SCH_3)_2]$ (1)

Ethanolic solutions (25 mL) of dimethyl *N*-cyanodithioiminocarbonate (0.235 g, 1.607 mmol) and triphenyltin chloride (0.619 g, 1.607 mmol) were mixed together at room temperature. A white precipitate is quickly obtained, which is then filtered off after 2 h stirring. After 4 days of slow evaporation at room temperature, colorless crystals, suitable for an X-ray crystallographic analysis, were grown from the filtrate and were finally characterized as **1** (0.503 g, 59% yield).

^1H-NMR ($CDCl_3$, 300 K): δ=0.96 (m, 6H, S-C*H*$_3$), 7.42 (m, 9H, C*H*, Ph), 7.64 (m, 6H, C*H*, Ph). $^{13}C\{^1H\}$ ($CDCl_3$, 300 K): δ=193.6 ($(CH_3S)_2$*C*=N-), 137.3 (Ph-*C*), 136.1 (Ph-*C*), 130.4 (Ph-*C*), 129.1 (Ph-*C*), 112.2 (N≡*C*-N=), 16.0 (S*C*H$_3$). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 300 K): δ=-47.8. δ=$^{119}Sn\{^1H\}$ NMR (toluene-d8, 300 K): δ=-50.9. IR (ATR, cm^{-1}): 3055 (w), 2991 (w), 2917 (w), 2202 (s), 1476 (s), 1426 (s), 1307 (m), 950 (m), 1070 (m), 1023 (m), 998 (m), 732 (s), 696 (s), 563 (m). Anal. Calcd. for $C_{22}H_{21}ClN_2S_2Sn$ (531.71): C 49.70, H 3.98, N 5.27; S 12.06. Found: C 49.69; H 4.15; N 5.33; S 10.89.

X-ray crystallography

A single colorless prism-shaped crystal with dimensions 0.50×0.20×0.12 mm^3 of **1** was selected and used for data collection using a Bruker D8 Venture triumph Mo diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at T=100 K. Data were measured using MoK_α radiation (λ=0.71073 Å). The total number of runs and images was based on the strategy calculation from the program APEX2 (Bruker, 2014). Cell parameters were retrieved and refined using the SAINT software (Bruker, 2014). Data reduction was performed using the SAINT software which corrects for Lorentz polarization. The structure was solved by direct methods using the SHELXT structure solution program (Sheldrick, 2015a) and refined by full matrix least squares on F^2 using SHELXL (Sheldrick, 2015b) with the aid of the Olex2 program (Dolomanov et al., 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The dimethyl *N*-cyanodithioiminocarbonate ligand was found disordered over two positions with occupation factors equal to 0.5.

CCDC 1472466 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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