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^{1}H and ^{13}C NMR of 2,2′-Bipyridine Adducts with Butyltin(IV) Trichloride and Tin(IV) Tetrachloride, and Tetrabromide

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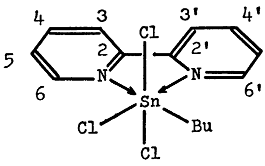
Synopsis. ^{1}H and ^{13}C NMR spectra of 2,2′-bipyridine adducts of butyltin(IV) trichloride and tin(IV) tetrachloride and -bromide have been measured in *N,N*-dimethylacetamide. On the basis of the chemical shifts of the ^{13}C nucleus and spin-spin coupling constants of the $^{117/119}$Sn with the ligand ^{1}H and ^{13}C nuclei the configuration of the adducts and the nitrogen-tin coordination bond are discussed.

Spin-spin coupling constants between the ligand atoms and the metal nucleus of complexes give important informations about the metal-ligand bond. To date, however, there have been only a few reports$^{1-3)}$ on the coupling constants between $^{117/119}$Sn nuclei and ligand protons measured in tin(IV) halide adducts of organic ligands, and tin couplings with ligand ^{13}C nuclei of the adducts have never been measured. Recently we have observed the couplings between the tin nuclei and the protons attached to the carbons adjacent to the coordinating nitrogen atoms in the 2,2′-bipyridine (bpy) adduct of butyltin trichloride.$^{2)}$ This paper reports ^{1}H and ^{13}C NMR data of bpy adducts of butyltin trichloride and tin tetrachloride and tetrabromide in *N,N*-dimethylacetamide.

As described previously,$^{2)}$ the bpy adduct of $BuSnCl_3$ is monomeric and a non-electrolyte in acetonitrile. Essentially the same situation is expected in *N,N*-dimethylacetamide, because the adduct in this solvent shows quite similar ^{1}H NMR spectral behavior to the observations in acetonitrile solution both in the absence and in the presence of excess bpy. The figure indicates the ^{13}C NMR spectrum of the bpy adduct of $BuSnCl_3$ in *N,N*-dimethylacetamide. Signal assignment is facilitated by the ^{13}C NMR measurement with selective $\{^1H\}$–^{13}C decoupling of each bpy proton signal. This assignment is consistent with that of platinum(II)–bpy complexes.$^{4,5)}$ The occurrence of the doubly separated C(2,2′) and C(5,5′) signals is in agreement with the previously suggested configuration A, where the butyl group lies on the N–Sn–N plane of the hexa-coordinated complex.$^{2)}$



(A)

In the spectra of the hexa-coordinated bpy–SnX_4 (X=Cl or Br) adducts the signals were also unchanged by the addition of excess bpy, indicating no significant exchange between the complexed and free ligands on the NMR time scale in this solvent.

The ^{13}C signal assignment of the adducts, as well as their ^{1}H NMR data, is summarized in the table.

The C(2,2′) and C(6,6′) signals of free bpy move upfield and the others move downfield in the complexes. Although the same behavior concerning the direction of signal shift upon complexation was also detected in the platinum(II)-bpy complexes,$^{4,5)}$ the large upfield shift of C(2,2′) and C(6,6′) signals is noticeable in the present tin halide adducts (see Table). This is rather analogous to the signal shift in the protonation of pyridine (C(2,6), +7.8 ppm; C(3,5), −5.0 ppm; C(4), −12.4 ppm).$^{6)}$

As is apparent from the figure, each ^{13}C signal has satellites due to the spin-spin coupling with the tin nuclei, while the ligand proton coupling with the tin atom is detected only at the H(6,6′) signal.$^{2)}$ In the platinum(II)–bpy complexes all bpy ^{13}C signals also give satellites due to the coupling with the ^{195}Pt nucleus.$^{4,5)}$ However, a marked difference in the relative magnitudes of the coupling constants in these complexes can be noticed; the C(4,4′)–platinum coupling is extremely small (≈6 Hz) compared with the platinum couplings of the other ring carbons (26—32 Hz), while the C(4,4′)–tin coupling is rather larger than the C(3,3′) and C(5,5′) couplings. This larger C(4,4′) coupling observed in the tin halide adducts may be indicative of a

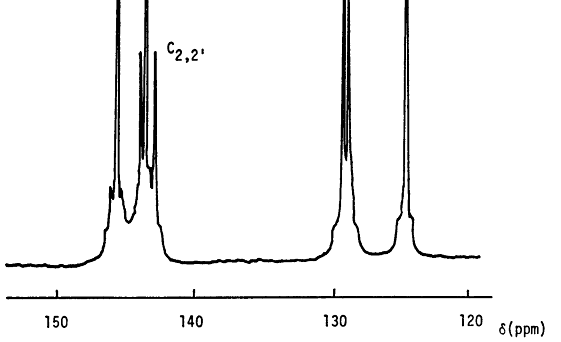


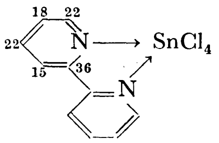
Figure. The ^{13}C NMR spectrum of $BuSnCl_3 \cdot bpy$ in *N,N*-dimethylacetamide at 32 °C.

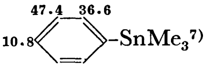
TABLE. ^{1}H AND ^{13}C NMR CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS ($^{117/119}$Sn–^{1}H AND $^{117/119}$Sn–^{13}C) (Hz)[a] FOR 2,2′-BIPYRIDINE ADDUCTS OF Tin(IV) HALIDES IN *N,N*-DIMETHYLACETAMIDE

	^{1}H Resonances[b]					^{13}C Resonances[c]						
	$H_{3,3'}$	$H_{4,4'}$	$H_{5,5'}$	$H_{6,6'}$		$C_{2,2'}$		$C_{3,3'}$	$C_{4,4'}$	$C_{5,5'}$		$C_{6,6'}$
bpy	8.48	7.94	7.44	8.72		156.2		121.0	137.5	124.5		149.8
$SnCl_4 \cdot$bpy	9.35	8.84	8.38	9.66 (34)		142.1 (36)		125.3 (15)	145.0 (22)	129.7 (18)		145.0 (22)
$SnBr_4 \cdot$bpy	9.39	8.87	8.46	9.81 (38)		141.1 (e)		125.4 (16)	144.1 (25)	129.5 (18)		145.3 (23)
$BuSnCl_3 \cdot$bpy[d]	9.13	8.63	8.18	9.84 (38)	9.21 (11)	142.8 (15)	144.1 (e)	124.5 (20)	143.6 (22)	128.4 (24)	128.9 (e)	145.5 (22)

a) Shown in parentheses. b) Measured at 24 °C. c) Measured at 32 °C. d) For ^{1}H NMR data in Ref. (2).
e) Could not be obtained since the signals were obscured by other signals.

significant π-interaction of bpy with the tin atom. This is in contrast with the fact that in trimethylphenyltin having a covalent aryl–tin bond the coupling between the tin and para-carbon nuclei is small;[7] here the phenyl-metal π-interaction may be small, as deduced in phenylplatinum derivatives.[8]





The tin–H(6,6′) or –carbon coupling constants of the $SnBr_4$ adduct are larger than those of the $SnCl_4$ adduct, indicating stronger Lewis acidity of $SnBr_4$. This is consistent with the result that stability constants of the $(CH_3)_2SnX_2$–bpy complexes increase in the order of X=Cl<Br<I.[9]

Directly bonded ^{13}C–^{1}H coupling constants of bpy obtained from the measurements without proton decoupling are larger in the adduct compared with those of the free ligand as follows.

	$^1J(^{13}C-^1H)$ (Hz)			
	$C_{3,3'}$–H	$C_{4,4'}$–H	$C_{5,5'}$–H	$C_{6,6'}$–H
Free bpy	170	163	163	178
$BuSnCl_3 \cdot$bpy	172	171	174	188

This is explainable as due to an increase of s-character in the C–H bond upon the adduct formation. The same behavior was reported in the directly bonded ^{13}C–^{1}H couplings on protonation of nicotinamide.[10]

Experimental

Materials. The preparation of $BuSnCl_3 \cdot$bpy was described previously.[2] $SnX_4 \cdot$bpy (X=Cl and Br) were prepared as white needles by mixing SnX_4 with an equimolar amount of bpy in acetonitrile. $SnCl_4 \cdot$bpy. Mp>300 °C. Found: C, 29.07; H, 2.00; N, 7.00%. Calcd for $C_{10}H_8N_2Cl_4Sn$: C, 28.82; H, 1.93; N, 6.72%. $SnBr_4 \cdot$bpy. Mp >300 °C. Found: C, 20.34; H, 1.34; N, 4.88%. Calcd for $C_{10}H_8N_2Br_4Sn$: C, 20.20; H, 1.36; N, 4.71%.

NMR Measurements. The ^{1}H NMR spectra were measured at 24 °C as described elsewhere.[1] The ^{13}C NMR spectra were obtained at 25.15 MHz using the pulse Fourier transform technique with a JEOL PS 100 spectrometer, an FT-100 FT unit, a DP-1 pulse programmer, and an EC-100 computer. ^{13}C chemical chifts in ppm were measured relative to TMS as an internal standard at 32 °C.

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