

Tin-119 N.M.R. Investigation of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$; Large Two-bond Tin–Tin Coupling Constant between *trans*-Disposed Ligands

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^{119}Sn Fourier transform n.m.r. studies of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ have revealed its stereochemical rigidity and a large two-bond tin–tin coupling constant, ${}^2J(^{119}\text{Sn}-^{117}\text{Sn})$, for the *trans*-disposed trichlorostannato ligands, the reduced value of which, ${}^2K(\text{SnSn})_{\text{trans}}$, $806.0 \times 10^{21} \text{ cm}^{-3}$, is the largest among analogous transition metal–tin complexes.

We have shown recently that Fourier transform ^{119}Sn n.m.r. spectroscopy elucidates clearly the co-ordination number of the trichlorostannato ligand and the stereochemical fluxionality of rhodium–tin complexes in hydrochloric acid solution.¹

Herein we report on the ^{119}Sn n.m.r. spectrum of a yellow solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and a 10 fold amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 3 M hydrochloric acid (Figure 1).

The well resolved spectrum shows the diamagnetic nature of

Table 1. ^{119}Sn N.m.r. data for some transition metal-tin complexes.

Complex	$\delta(^{119}\text{Sn})/\text{p.p.m.}$	$^2J(^{119}\text{Sn}-^{117}\text{Sn})/\text{Hz}$
d^8 $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$	-34.6 ^a	2 364 ^a (<i>cis</i>) 12 862 ^a (<i>trans</i>)
d^8 $[\text{Rh}(\text{SnCl}_3)_3\text{Cl}_3]^{3-}$	-411.1 ^b	2 804 ^b
d^8 $[\text{Rh}(\text{SnCl}_3)_5]^{4-}$	8.5 ^b	3 634 ^b
d^8 $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$	-142 ^c	6 230 ^c
	-133.4 ^d	6 387 ^d
d^8 $[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$	-387 ^c	2 485 ^c

^a This work. ^b Ref. 1. ^c J. H. Nelson, V. Cooper, and R. W. Rudolph, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 263; *ibid.*, 1980, **16**, 587. ^d H. Moriyama, T. Aoki, S. Shinoda, and Y. Saito, unpublished results.

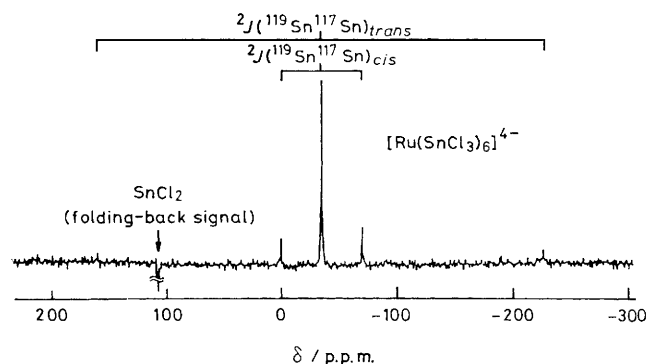


Figure 1. ^{119}Sn N.m.r. spectrum of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ at 25 °C, accumulated with a 90° pulse and 1.0 s interval at 33.34 MHz after mixing the solution for 1 day. Chemical shifts are referred to Me_4Sn .

the solution. The rapid reduction of ruthenium(III) by tin(II) chloride is evident by the fact that the corresponding amount of free Sn^{IV} species is always present in the solution.

The spectrum consists of one main peak, two types of satellite peak with a relative intensity of 4:1, and a folding-back signal due to the excess amount of free tin(II) chloride. The spectra for the same sample at elevated temperatures showed that neither intra- nor inter-molecular scrambling occurred at least up to 70 °C (Figure 2). Stereochemical rigidity of the ruthenium(II)-tin(II) complex is in sharp contrast with the fluxional behaviour of the isoelectronic rhodium(III)-tin(II) complexes.¹

The observed relative intensity of the satellite peaks compared with the main peak (21.8%) agrees well with the value

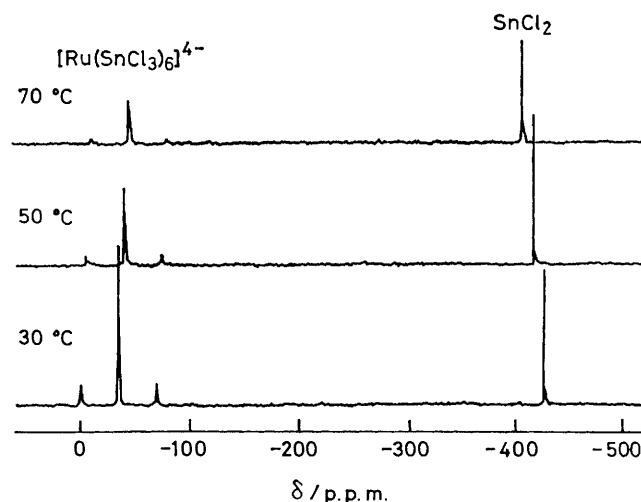


Figure 2. ^{119}Sn N.m.r. spectra of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ at elevated temperatures. The sample and the n.m.r. conditions are the same as for Figure 1.

(22.4%) calculated statistically from the natural abundances of ^{119}Sn (8.6%) and ^{117}Sn (7.6%) nuclei in hexakis (tin) complexes. Moreover, an octahedral structure is deduced from the satellite intensity ratio of 4:1. $[\text{NMe}_4]_4[\text{Ru}(\text{SnCl}_3)_6]$ was isolated and identified from the solution.²

Table 1 summarizes the tin chemical shifts and the two-bond tin-tin coupling constants studied for analogous transition metal-tin complexes. $^2J(\text{SnSn})_{trans}$ of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ is not only significantly larger than $^2J(\text{SnSn})_{cis}$, but is also the largest among these complexes.†

$^2J(\text{XY})$ values of transition metal complexes for various nuclei are shown in Table 2. Since the reduced spin-spin coupling constant, $K(\text{XY}) = (2\pi/\hbar\gamma_X\gamma_Y) \cdot J(\text{XY})$, is more appropriate as a comparison of the magnitude of different nuclei, the calculated 2K values are also listed. The reduced two-bond coupling constant between the *trans*-disposed tin ligands is the largest.

In view of the predominant contribution of the Fermi contact interaction to nuclear spin-spin coupling in transition metal complexes,³ the bonding properties of the $\text{Sn}^{II}-\text{M}-\text{Sn}^{II}$

† In transition metal-tin-phosphine complexes, larger $^2J(\text{SnSn})_{trans}$ values are known; P. S. Pregosin, *Chimia*, 1981, **35**, 49.

Table 2. Two-bond nuclear spin-spin coupling constants between various nuclei in transition metal complexes.

X	Y	$^2J(\text{XY})_{cis}/\text{Hz}$	$^2K(\text{XY})_{cis}/10^{21}\text{cm}^{-3}$	$^2J(\text{XY})_{trans}/\text{Hz}$	$^2K(\text{XY})_{trans}/10^{21}\text{cm}^{-3}$	Ref.
^{13}C	^{13}C	3.2	(0.42)	35	(4.6)	a
^{31}P	^1H	-17.5	(-0.36)	+158.5	(+3.26)	b
^{31}P	^{13}C	9	(0.74)	104	(8.50)	b
^{31}P	^{15}N	3	(0.61)	61	(12.4)	b
^{31}P	^{19}F	31.6	(0.69)	140	(3.06)	b
^{31}P	^{31}P	-8.0	(-0.41)	+610	(+30.9)	b
^{31}P	$^{119,117}\text{Sn}^e$	214	(12.1)	4 188	(235.9)	b
^{31}P	^{119}Hg	397	(45.6)	3 879	(445.9)	b
^{119}Sn	^1H	—	(—)	1 740	(38.8)	c
^{119}Sn	^{117}Sn	2 364	(148.1)	12 862	(806.0)	d

^a $^2J_{cis}$: S. Aime and D. Osella, *J. Chem. Soc., Chem. Commun.*, 1981, 300; $^2J_{trans}$: M. Tachikawa, S. I. Richter, and J. R. Shapley, *J. Organomet. Chem.*, 1977, **128**, C9. ^b Ref. 3, p. 114. ^c K. A. Ostojka Starzewski, H. Ruegger, and P. S. Pregosin, *Inorg. Chim. Acta*, 1979, **36**, L445. ^d This work. ^e Average of ^{119}Sn and ^{117}Sn nuclei.

species warrants attention, as the complex may be regarded as a metal-cluster compound. The *trans*-labilizing effect of the trichlorostannato ligand,⁴ which has been related to the catalytic activity of some transition metal-tin complexes,⁵⁻⁷ is also an important subject, which might be made clearer by quantum chemical bond analysis⁸⁻¹⁰ on nuclear spin-spin coupling constants.

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