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X-Ray Crystal Structure and Multinuclear Tin Fourier Transform N.M.R. Studies of the Anion $[Ru(SnCl_3)_5Cl]^{4-}$: the First Directly Measured ^{99}Ru Spin–Spin Coupling Constant

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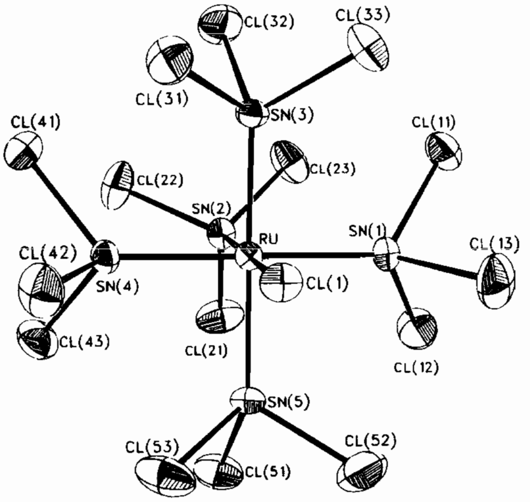

Fig. 1. ORTEP diagram of the $[Ru(SnCl_3)_5Cl]^{4-}$ anion (50% ellipsoids). Selected bond lengths (Å) and bond angles (°) are: Ru–Sn(1), 2.579(1); Ru–Sn(2), 2.553(2); Ru–Sn(3), 2.564(1); Ru–Sn(4), 2.586(1); Ru–Sn(5), 2.586(1); Ru–Cl(1), 2.468(4); ∠ Cl(1)–Ru–Sn(2), 179.5(1); ∠ Sn(1)–Ru–Sn(4), 179.00(6); ∠ Sn(3)–Ru–Sn(5), 167.01(7).

Interest remains high in the catalytic activity of trichlorostannate(II) complexes of the platinum metals, which have been used for a variety of reactions including hydrogenation [1], hydroformylation [2] and isomerisation [3] of olefins, dehydrogenation of alcohols [4], and the Water-Gas Shift reaction [5, 6]. Some rhodium [7, 8] and platinum [9] complexes have been the most well-characterized. We report here the full characterization of the octahedral ruthenium(II) anion [10, 11] $[Ru(SnCl_3)_5Cl]^{4-}$, which reveals a tin–ruthenium N.M.R. coupling, the first time that coupling to a ruthenium nucleus has been observed. The tetraethylammonium salt was isolated with two acetonitrile solvate molecules.

Crystal data: $C_{32}H_{80}Cl_{16}N_4RuSn_5 \cdot C_4H_6N_2$, orthorhombic, space group $P2_1ca$ (non standard setting of $Pca2_1$) a = 19.796(5), b = 13.882(2), c = 24.772(2), U = 6807.5 Å^3, Z = 4, D_m = 1.835, D_c = 1.833, μ = 27.4 cm^{-1} for Mo-$K_{\alpha 1}$ radiation. The 6587 independent reflections ($2\theta \leqslant 50°$) were measured on an Enraf-Nonius CAD4-F diffractometer using a crystal 0.25 × 0.35 × 0.40 mm. The structure was solved by direct methods and, after application of an absorption correction, all non H atoms were located from difference maps. The H atom contributions to structure factors were included from calculated positions and not refined. Convergence was reached at R = 0.035.

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TABLE I. Tin N.M.R. Data for the $[Ru(SnCl_3)_5Cl]^{4-}$ Anion.[a,b]

$\delta\ ^{119}Sn_{eq} = -167.9$ ppm[c]
$\delta\ ^{119}Sn_{ax} = -149.2$ ppm[c]

Coupling constants/Hz	$^{119}Sn-^{117}Sn$[c]	$^{119}Sn-^{117}Sn$[d]	$^{117}Sn-^{119}Sn$[e]	$^{115}Sn-^{119}Sn$[f]	$^{115}Sn-^{117}Sn$[f]
$^2J(Sn_{eq}-Sn_{eq})$*trans*	21254(6)	21236(12)	21243(6)	19485(6)	18624(6)
$^2J(Sn_{eq}-Sn_{eq})$*cis*	2938(2)	2930(2)	2935(2)	2694(2)	2568(2)
$^2J(Sn_{eq}-Sn_{ax})$*cis*	2581(2)	2583(2)	2578(2)	2361(2)	2266(2)
	2582(2)	2578(2)	2577(2)		
$^1J(Sn_{eq}-^{99}Ru)$[g]	846(2)	848(2)	810(2)	–	–

[a]Chemical shifts downfield relative to $SnMe_4$ as external standard. [b]Estimated errors in parentheses. [c]From ^{119}Sn spectrum 37.3 MHz. [d]From ^{119}Sn spectrum 15.02 MHz. [e]From ^{117}Sn spectrum 35.6 MHz. [f]From ^{115}Sn spectrum 32.7 MHz. [g]Sn_{eq} refers to observed tin nucleus.

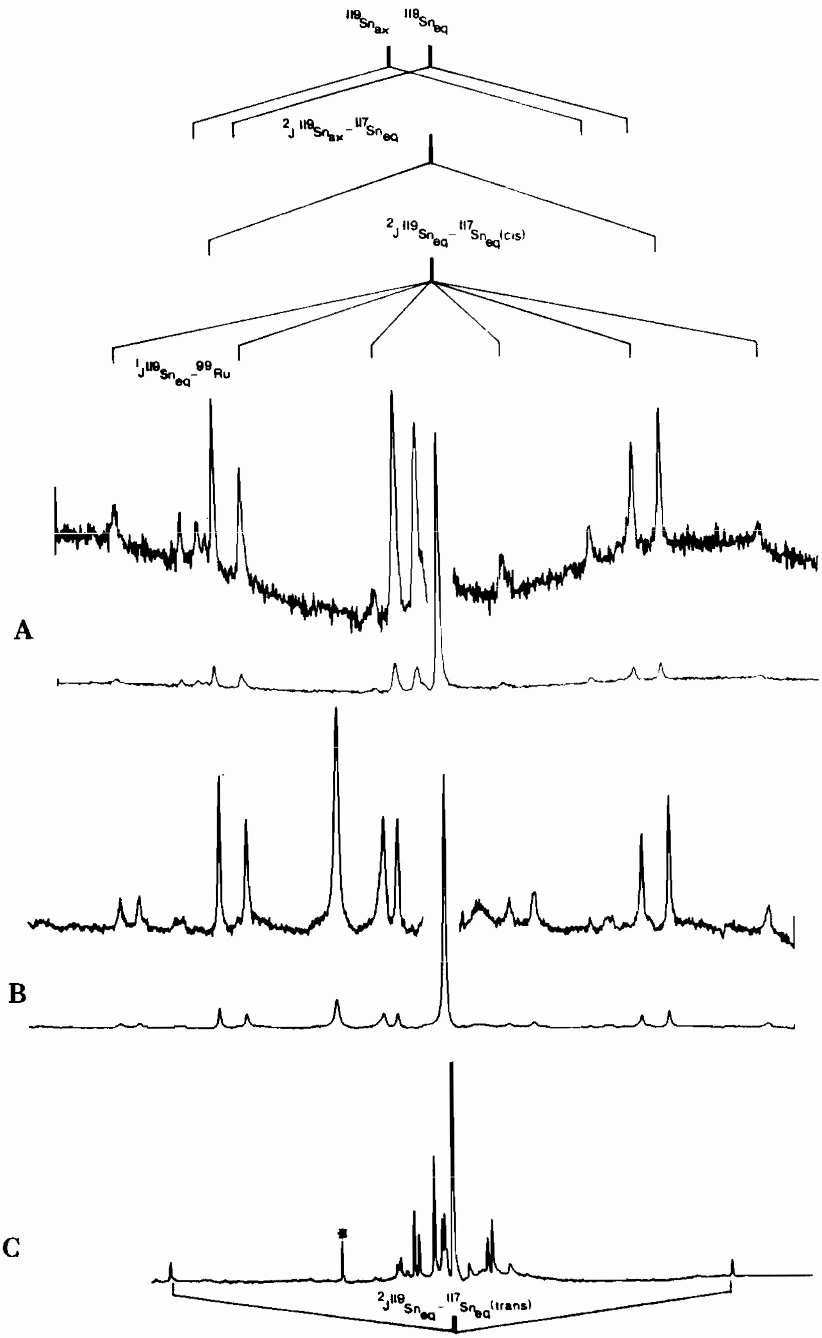

Fig. 2. ^{119}Sn F.T. N.M.R. spectra of $(NEt_4)_4[Ru(SnCl_3)_5Cl]$ in nitromethane, at ambient temperature. A) 15.02 MHz, 5000 Hz sweepwidth, 694,000 scans; at two amplitudes. B) 37.3 MHz, 5000 Hz sweepwidth, 118,000 scans; at two amplitudes. C) 37.3 MHz, 30,000 Hz sweepwidth, 4702 scans; * impurity.

The anion (Fig. 1) shows near idealized C_s symmetry, except for a slight distortion from linearity along the Sn(5)–Ru–Sn(3) axis; the remaining angles about Ru are very close to 90°. The Ru–Sn bond lengths are rather shorter than expected, presumably due to dπ–dπ interactions, as invoked for other transition metal–$SnCl_3$ complexes [12]. The Ru–Cl distance is greater than usually observed, and is attributed to the high *trans*-influence of the $SnCl_3^-$ ligand [13].

The ^{119}Sn F.T. N.M.R. spectra (Fig. 2) show that the same structure is retained in solution: the two main resonances are assigned to the unique axial tin, and the four equational ones that become equivalent in solution. There are also three sets of satellites, centred on the equatorial resonance, that are due to coupling to ^{117}Sn; the large $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ coupling constants (Table I) are similar to those found in platinum(II)–$SnCl_3$ complexes [9, 14], and that for $^2J(^{119}\text{Sn}_{eq}-^{117}\text{Sn}_{eq})$ *trans* represents the largest recorded two-bond coupling constant. The axial resonance shows the expected one set of satellites. Because of the proximity of chemical shifts, second order effects are seen in the $^{119}\text{Sn}_{ax}-^{119}\text{Sn}_{eq}$ coupling. It is thus observed as the inner two resonances of an AB pair (outer lines too weak to observe) when recorded at 37.3 MHz, but only as a broad, unresolved singlet at 15.02 MHz. Confirmation of these assignments is afforded by the ^{117}Sn N.M.R. spectrum, which is identical except for the $^{117}\text{Sn}_{ax}-^{117}\text{Sn}_{eq}$ coupling constant. A ^{115}Sn F.T. N.M.R. spectrum reveals all satellites as doublets due to coupling to both ^{119}Sn and ^{117}Sn, and the values of these constants agree with those calculated from the gyromagnetic ratios. Intensities of all the lines in the ^{119}Sn, ^{117}Sn, and ^{115}Sn spectra agree well with the calculated values.

Figure 2 also reveals coupling to ^{99}Ru ($I = 5/2$); four of the expected six lines are seen in the 15.02 MHz spectrum, the other two being obscured by ^{117}Sn satellites. The couplings to ^{119}Sn (846 Hz) and ^{117}Sn (810 Hz) are the first reported for the ^{99}Ru nucleus (12.7% natural abundance); its low quadrupole moment (+0.076 cm^2), and the high symmetry of the anion, allow observation of this effect. Coupling to ^{101}Ru ($I = 5/2$) with the larger quadrupole moment (+0.44) is not seen, presumably because of line-broadening.

Acknowledgements

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