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A Mössbauer Spectroscopic Study of [Phthalocyaninato Tin(IV) Tetracarbonyl Iron(0)]

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Abstract

The action of $Na_2Fe(CO)_4$ and bis(chloro)phthalocyaninato tin(IV) yields phthalocyaninato tin(IV) tetracarbonyl iron(0). Mössbauer spectroscopic studies on the product indicate no change in formal oxidation state need be invoked to account for the formation of the metal–metal bond.

Introduction

Recently a report of the crystal structure of [2,3,7,8,12,13,17,18 octaethylporphyrinato tin(II) tetracarbonyl iron(0)] (**A**) has appeared [1]. The assignment of the valence state (II) to the tin atom was based on considering [(oep)Sn(II)]** as a σ-donor ligand, in conjunction with this being the 'expected' behaviour as reduction of diorganometal dichlorides. $R_2M(IV)Cl_2$ (M = Ge, Sn, Pb) by $Na_2Fe(CO)_4$ produced dimeric $[R_2M(II)Fe(CO)_4]_2$ complexes [2, 3, 4]. It was a pity that although the authors gave ^{57}Fe Mössbauer data for their complex they did not present any ^{119}Sn data.

In this laboratory we have been interested in the properties of metal phthalocyanine complexes and have prepared [phthalocyaninato tin(IV) tetracarbonyl iron(0)], $[(Pc)SnFe(CO)_4]$** (**B**).

We report here its preparation and its ^{119}Sn and ^{57}Fe Mössbauer spectra and discuss these in relation to the formulation and structure of **A** [1].

Results and Discussion

The ^{57}Fe and ^{119}Sn Mössbauer data for compound (**B**) are presented in Table I. The ^{57}Fe Mössbauer data are similar to those found for compound (**A**). These data fit the quasi-linear correlation between quadrupole splitting and isomer shift reported by Collins and Petit [5] for iron atoms that possess a C_{3v} symmetry. Although the crystallographic symmetry of **A** does not have an iron atom with this 'exact' symmetry, the electronic environment of the iron atom could be of this symmetry. The trends in isomer shift values were interpreted in terms of a dominant σ-interaction synergically buttressed by π-bonding [6]. This suggests that the iron atom receives electron density from the fifth ligand (here it would be the tin atom). However, as will be discussed below, this simplification is dangerous.

Clearly the iron atoms have isomer shift data in the zero oxidation state region. The ^{119}Sn isomer shift data for our complex (**B**) is much lower than that found for the oxygen sensitive phthalocyaninato tin(II) [7] and in the region normally associated with organometallic tin(IV) complexes. Indeed it is higher than those of the more usual phthalocyaninato tin(IV) halides [7], as would be expected for a material

TABLE I. ^{57}Fe and ^{119}Sn Mössbauer Parameters of $(Pc)SnFe(CO)_4$ and Relevant Related Materials

Complex	T (K)	^{57}Fe			^{119}Sn		
		δ (mm s^{-1})[a]	Δ (mm s^{-1})	Γ (mm s^{-1})	δ (mm s^{-1})[b]	Δ (mm s^{-1})	Γ (mm s^{-1})
$(Pc)SnFe(CO)_4$	77	−0.10(1)	2.26(1)	0.34(1)	1.32(1)	1.37(1)	0.94(2)
$(oep)SnFe(CO)_4$[c]	95	−0.081	2.27	0.31			
	297	−0.154	2.23	0.22			
$(Pc)SnCl_2$[d]	77				0.30	0.99	
$Fe(CO)_5$[e]	77	−0.09	2.57				
$(Pc)Sn$[d]	77				2.88	1.44	

[a] Relative to natural iron at 298 K. [b] Relative to SnO_2 at 298 K. [c] Ref. 1. [d] Ref. 7. [e] Ref. 10.

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**(oep) = [2,3,7,8,12,13,17,18]octaethylporphyrin dianion; (Pc) = phthalocyaninato dianion.

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containing a tin–iron bond [8, 9]. It is dangerous in assigning formal oxidation states to such complexes but Mössbauer spectroscopists usually assign an oxidation state of IV to tin complexes with isomer shifts less than 2.1 mm s^{-1} (the shift of α-tin). In relation to this point ^{119}Sn Mössbauer data for a series of $[R_2SnFe(CO)_4]_2$ complexes [3] have isomer shifts in the range 1.86–2.00 mm^{-1} and quadrupole splittings in the range 2.51–3.13 mm s^{-1} (claimed by Barbe *et al.* [1] to be Sn(II) materials), we feel are better classed as Sn(IV) complexes. The bonding in the latter complexes has been suggested to be synergic in tin → metal and metal–tin (d → p) π bonding along the tin metal axis [3].

Hence the (pc)Sn(IV) moiety can best be considered to have exchanged the two negatively charged chloride ligands for the doubly charged $[Fe(CO)_4]^{2-}$ ligand.

Thus the reactions:

$$(Pc)SnCl_2 + Na_2Fe(CO)_4 \longrightarrow (Pc)SnFe(CO)_4 + 2NaCl$$

can best considered not to involve a change in oxidation state. It seems to us reasonable to suppose that the oxidation state of the tin atom in complex A is also (IV).

Experimental

The ^{57}Fe and ^{119}Sn Mössbauer spectra were recorded as described previously [11, 12]. Infra-red spectra were recorded as Nujol maltols in the region 2200 cm^{-1}–1800 cm^{-1} on a Perkin Elmer 225 spectrophotometer using NaCl windows. Visible spectra were recorded on a Beckman DU-7 spectrophotometer over the range 350–850 nm.

Preparation of [(Pc)SnFe(CO)$_4$]

The title compound was prepared via the action of $Na_2Fe(CO)_4$ on $(Pc)SnCl_2$ [13]. $Fe(CO)_5$ (0.1 ml, 0.71 mmol) was added to a suspension of sodium amalgum in dry THF (180 ml) under dry nitrogen and stirred for 5 h in the dark. $(Pc)SnCl_2$ (0.5 g, 0.71 mmol) was then added and the mixture stirred for a further 24 h at room temperature.

The crude $(Pc)SnFe(CO)_4$ was then filtered under dry nitrogen and the THF removed under vacuo. The product was purified via column chromatography (activated neutral alumina 120 mm × 12 mm): eluant THF. Evaporation of the eluate resulted in a green microcrystalline material. Yield 83 mg (14%), λ_{max} (THF) 710 nm. *Anal.* Calc. for $C_{36}H_{16}N_8O_4FeSn$: C, 54.06; H, 2.00; N, 14.02. Found: C, 54.1; H, 1.9; N, 13.8%.

The infrared spectrum recorded for the above compound is consistant with local C_{3v} symmetry for the $Fe(CO)_4$ fragment. A^1 (2027 cm^{-1}), A^1 (1947 cm^{-1}) and E (1917 cm^{-1}).

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