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SYNTHESIS OF FERROCENOPHANE AND [2] AND [3]FERROCENOPHANE-TIN CHLORIDE ADDUCTS AND THEIR MÖSSBAUER SPECTROSCOPIC STUDIES

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Adducts of tin-tetrachloride with [2]ferrocenophane were prepared by treating $SnCl_4$ with [2]ferrocenophane in hexane. The adducts were studied by means of ^{57}Fe- and ^{119}Sn-Mössbauer spectroscopy and other physicochemical measurements. An anomalously large quadrupole splitting value found in the ^{57}Fe-Mössbauer spectroscopy of the red-orange adduct prepared from [2]ferrocenophane (3.49 mm s^{-1} at 78 K, 3.45 mm s^{-1} at 300 K) suggests the presence of a direct chemical bonding between Fe and Sn atoms, whereas the dark green adducts prepared from ferrocene and [3]ferrocenophane consist of ferrocenium and [3]ferrocenophanium cations, respectively.

Although it has been found by R. M. G. Roberts et al. that an unstable adduct of ferrocene with mercuric chloride, $Fe(Cp)_2 \cdot 7HgCl_2$, shows an anomalously large quadrupole splitting (Q. S.) value (3.09 mm s^{-1} at 78 K) suggesting the presence of iron-mercury bonding,[1)] there are few compounds in which iron atoms in ferrocene derivatives are coordinated with other metallic atoms as in the case of ruthenocene tin chloride. They have also reported that a large Q. S. value (2.72 mm s^{-1}) is found in the adduct, $Fe(Cp)_2 \cdot HAlCl_4$, in which a strong interaction between iron and hydrogen atoms is assumed to cause the cyclopentadienyl rings to tilt.[2)]

On the other hand, [2]ferrocenophanes are known to have a tilted cyclopentadienyl-ring structure, in which each Cp ring declines by 23° according to the X-ray structural studies.[3)] The facts suggested to us that we could synthesize a new stable adduct compound in which iron atoms can be easily coordinated with other metal atoms because of the "naked" structure of iron atoms' electrons, as in the case of ruthenocene metal adducts where the e_{2g} electrons of ruthenium atoms can afford to be coordinated with a vacant orbital of other metal atoms because the two Cp rings are well separated.

[2]Ferrocenophane and [3]ferrocenophane were prepared by the method reported by H. L. Lentzner and Watts,[4)] and A. Lüttringhaus and W. Kullick.[5)] The adduct of tin chloride with [2]ferrocenophane was prepared by the following method. To a solution of [2]ferrocenophane dissolved in dry hexane, a hexane solution of $SnCl_4$ was added in a nitrogen-filled dry-box equilibrated with P_2O_5, and the produced red-orange precipitates were filtered, washed with a large excess of hexane, and dried under vacuum.

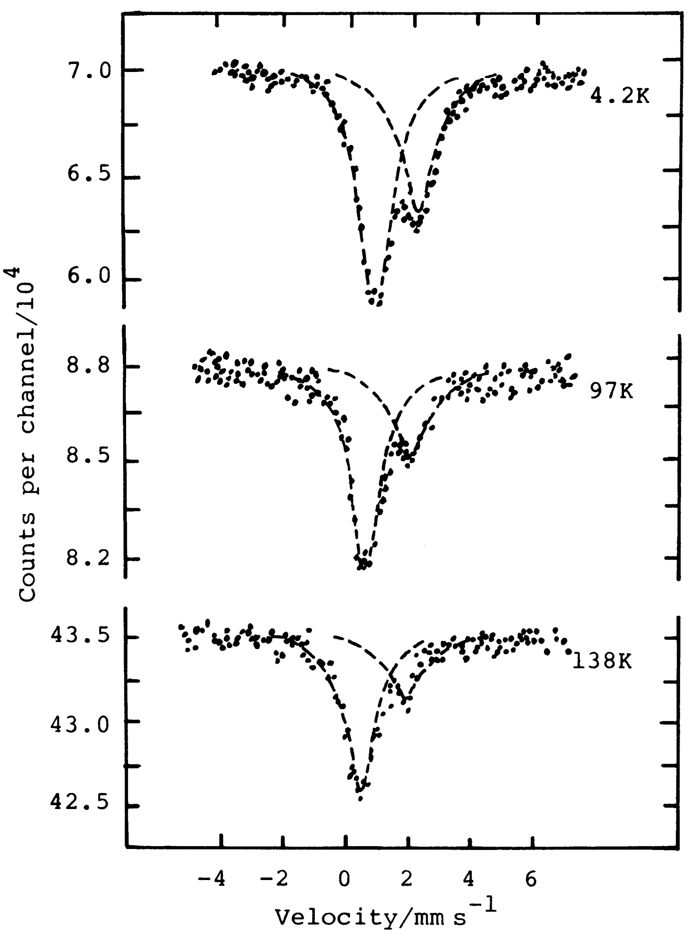

Fig. 1. ^{119}Sn-Mössbauer spectra of [2]ferrocenophane-$SnCl_4$ adduct at different temperatures.

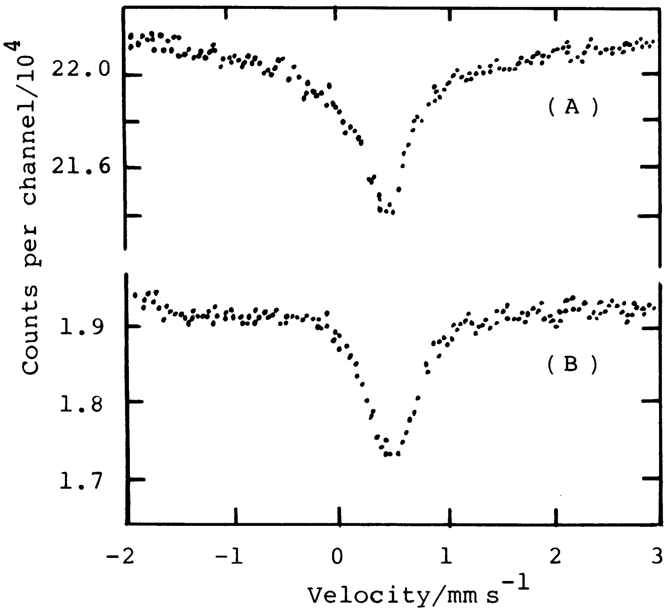

Fig. 2. ^{57}Fe-Mössbauer spectra of (A) ferrocene-$SnCl_4$ adduct and (B) [3]ferrocenophane-$SnCl_4$ adduct both at 78 K.

The purity of the adduct was confirmed by elemental analysis: Found: C, 23.41; H, 2.77; Sn, 29.07; Fe, 7.97 %. Calcd for $C_{24}H_{28}Fe_2Sn_3Cl_{12}O_2$: C, 23.19; H, 2.25; Sn, 28.67; Fe, 8.99 %. Reaction products of [3]ferrocenophane with $SnCl_4$ were obtained by using the same condition as in the case of [2]ferrocenophane, but the color of the precipitates was dark-green, characteristic of ferrocenium salts. Found: C, 27.43; H, 2.93; Sn, 26.13; Fe, 8.73 %. Calcd for $C_{52}H_{68}Fe_4Sn_5Cl_{20}O_6$: C, 26.96; H, 2.94; Sn, 25.64; Fe, 9.65 %. Reaction products of ferrocene with $SnCl_4$ were also obtained in the same condition. The dark-green precipitates were washed with hexane. Found: C, 20.10; H, 2.05; Sn, 28.85; Fe, 9.03 %. Calcd for $C_{26}H_{28}Fe_2Sn_3Cl_{12}O_4$: C, 19.58; H, 2.28; Sn, 29.05; Fe, 9.11 %.

The adduct of [2]ferrocenophane-$SnCl_4$ is hardly soluble in most organic solvents but soluble into dimethylformamide giving the original absorption spectrum of [2]ferrocenophane, while the other adducts are soluble into dimethylformamide and the resulting green-colored solutions give absorption spectra similar to that of a solution of ferrocenium salts.

^{57}Fe-Mössbauer measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode, while ^{119m}Sn-Mössbauer spectra were measured against a $Ca^{119m}SnO_3$ source. The velocity calibration was made by the resonance lines of an ^{57}Fe-enriched metallic iron absorber against the ^{57}Co(Pt) source. The isomer shift for ^{57}Fe was taken with respect to metallic iron and that for ^{119}Sn was described with respect to a

$BaSnO_3$ absorber. The experimental error of the isomer shift and quadrupole splitting values are estimated to be within 0.02 mm s^{-1}.

^{119}Sn-Mössbauer spectra of [2]ferrocenophane-tin chloride adduct, $[(C_2H_4Cp_2Fe)_2SnCl_2](SnCl_5)_2$-$2H_2O$ are shown in Fig. 1, where two kinds of chemical states of tin atoms are observed. Although the temperature dependences of the spectral area in both the components are different, the recoil-free fractions of both the tin atoms may be assumed to become approximately equal at lower temperatures. The component with higher I. S. corresponds to $(Cp')_2Fe$-$SnCl_2$-$Fe(Cp')_2{}^{2+}$-type tin species and the other broad component with a lower I. S. to a rather ionic $SnCl_5{}^-$-type tin(IV) species, from the similarity of the Mössbauer spectroscopic parameters found in tetravalent organotin or organometal-tin chlorides and hexachlorotin(IV) species, respectively. The areal intensity ratio of the two components at 4.2 K agrees with the proposed formula which is consistent with the elemental analysis data.

For the sake of comparison, ^{57}Fe- and ^{119}Sn-Mössbauer spectra of the adducts prepared from ferrocene and [3]ferrocenophane with tin tetrachloride are shown in Figs. 2 and 3, respectively. In the ^{57}Fe-Mössbauer spectra of both the adducts, a broad singlet peak is observed indicating that iron atoms are in the ferrocenium-like chemical state as expected from the dark-green color of the adducts. The ^{119}Sn-Mössbauer spectra show that there are three components ascribed to two kinds of Sn(IV)

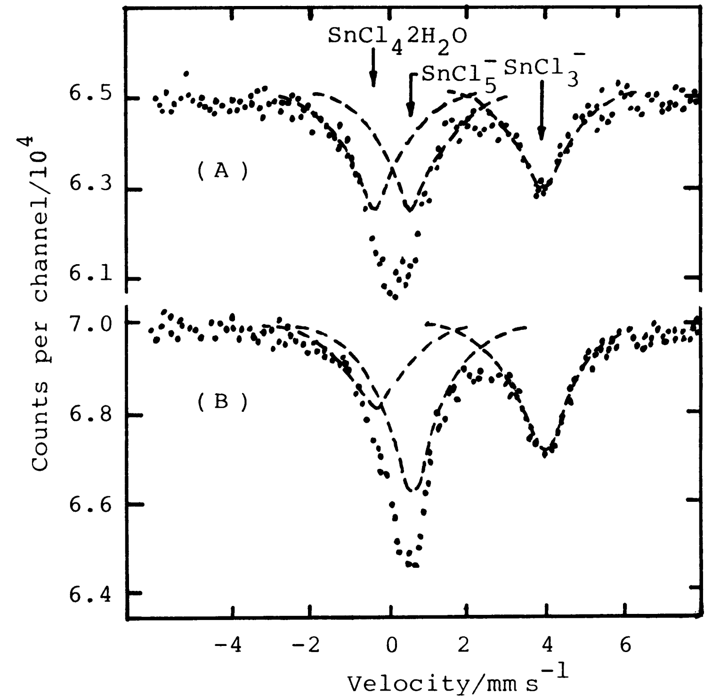

Fig. 3. ^{119}Sn-Mössbauer spectra of (A) ferrocene-$SnCl_4$ adduct and (B) [3]ferrocenophane-$SnCl_4$ adduct both at 78 K.

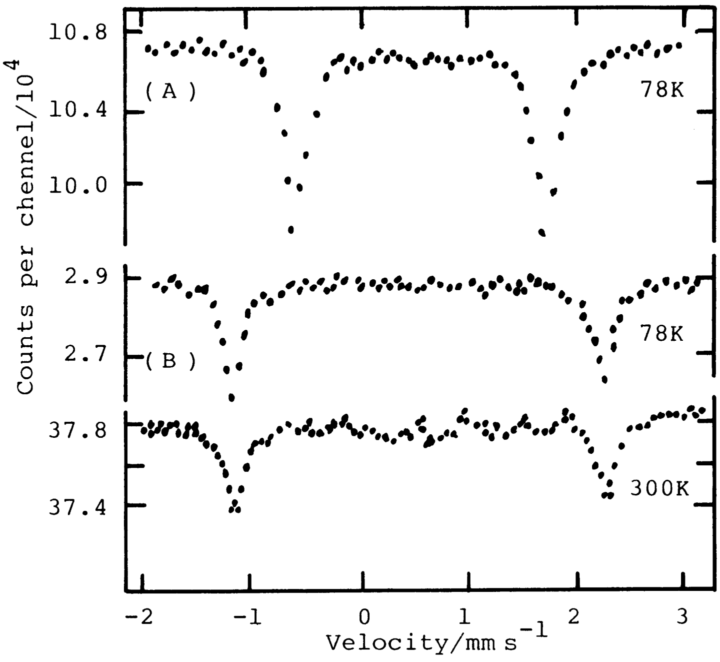

Fig. 4. ^{57}Fe-Mössbauer spectra of (A) [2]ferrocenophane and (B) [2]ferrocenophane-$SnCl_4$ adduct at the indicated temperatures.

species and to a kind of Sn(II) species. The results indicate that the adducts prepared from ferrocene and [3]ferrocenophane with tin tetrachloride are expressed as $[(C_5H_5)_2Fe^+]_2(SnCl_3^-)(SnCl_5^-)SnCl_4 \cdot 4H_2O$ and $[(C_5H_4)_2C_3H_6Fe^+]_4(SnCl_3^-)_2(SnCl_5^-)_2$-$SnCl_4 \cdot 6H_2O$, respectively, in accord with the elemental analysis data.

Figure 4 shows ^{57}Fe-Mössbauer spectra at various temperatures of the adduct, $[(C_2H_4Cp_2Fe)_2SnCl_2](SnCl_5)_2 \cdot 2H_2O$. An anomalously large Q. S. value (3.49 at 78 K) is found compared with the value of ferrocene derivatives which ranges from 2.2 to 2.4 mm s^{-1}. This large value cannot be explained sufficiently by assuming only an increased asymmetric parameter caused by the tilting Cp rings as in the case of [2]ferrocenophane. The results indicate that the essentially nonbonding electrons (e. g., e_{2g} electrons in ferrocene) should be coordinated to vacant orbitals of tin(IV) atoms, since the tilting Cp ring structure in this compound is considered to make the coordination easier. A similar coordination has been observed in Cp_2Ru-$Sn(Cl)_2$-$Ru(Cp)_2$ by Mann et al.,$^{6)}$ where the larger size of ruthenium atoms compared with iron atoms in ferrocene can afford to coordinate the e_{2g} electrons with tin orbitals in the ruthenocene adduct.

The magnetic susceptibility measurements show that the adduct $[(C_2H_4CpFe)_2$-$SnCl_2](SnCl_5)_2 \cdot 2H_2O$ is diamagnetic at temperatures from 78 K to 295 K, indicating no possibility of oxidation of [2]ferrocenophane to a ferrocenophanium cation.

The results obtained in the present studies all support the coordination bonds between iron atoms in [2]ferrocenophane moieties to the central tin atom. This suggests to us that other tilted Cp-ring structured ferrocene derivatives might also have possibilities to coordinate with several kinds of metal atoms through iron-metal bonding.

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