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^{119}Sn-Moessbauer Spectroscopic Studies of Tin(IV) Chloride Adducts of Ferrocenylruthenocene and Biruthenocene

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An orange colored stable adduct of $SnCl_4$ with biruthenocene was prepared by treating $SnCl_4$ with biruthenocene in a dry solution of benzene mixed with hexane, while a less stable adduct with ferrocenylruthenocene was obtained in the same procedure. Covalently bonded tin(IV) species were found in ^{119}Sn-Moessbauer spectroscopy of both the adducts. The results suggest the presence of a direct chemical bonding between Ru and Sn atoms in these adducts.

It has recently been reported that ^{57}Fe-Moessbauer spectra of $HgCl_2$ adducts of biferrocene and ferrocenylruthenocene show anomalously large quadrupole splitting (Q. S.) values (2.93 mm s^{-1} for biferrocene-$2HgCl_2$ and 2.99 mm s^{-1} for ferrocenylruthenocene-$5HgCl_2$, both at 78 K) suggesting a direct interaction between the Fe and Hg atoms in the adducts.[1,2] Much greater stability of biferrocene-$2HgCl_2$ and ferrocenylruthenocene-$5HgCl_2$ compared with ferrocene-$7HgCl_2$ was explained by assuming a chelation of the Fe-Fe and Fe-Ru atoms in biferrocene and ferrocenylruthenocene.

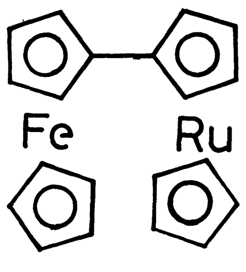
Ferrocene reacts with $SnCl_4$ giving a dark green colored ferricinium salt, whereas ruthenocene and [2]ferrocenophane react with $SnCl_4$ to give yellow and reddish orange adducts, respectively.[3,4] Based on the results of ^{119}Sn-Moessbauer spectroscopic studies of these adducts, covalently bonded tin(IV) species (isomer shift (I. S.) values, 2.08 mm s^{-1} and 2.14 mm s^{-1} both at 78 K, respectively) were found as in the case of organometallic tin(IV) compounds, suggesting the presence of a direct interaction between Ru-Sn and Fe-Sn atoms in the adducts. Although it was expected that biferrocene could provide a stable adduct of $SnCl_4$ by the aid of chelating effect of two iron atoms in biferrocene, it was shown that the reaction of biferrocene with $SnCl_4$ gave no adduct but a paramagnetic ferricinium salt, based on the results of ^{57}Fe- and ^{119}Sn-Moessbauer studies; i.e., biferrocene was found to be monooxidized by $SnCl_4$ giving a trapped-valence state.[4]

It has been reported that the cyclopentadienyl (Cp) rings are separated by 3.32 Å from each other in a ferrocene molecule and 3.68 Å in a ruthenocene molecule.[5,6] Therefore, it is expected that ferrocenylruthenocene and biruthenocene might provide stable adducts of $SnCl_4$, because these binuclear metallocenes have a large separation of Cp-rings in ruthenocene moieties. It is also expected that biruthenocene gives more stable adducts with $SnCl_4$ than ruthenocene-$1.5SnCl_4$ because of a chelating effect of Ru-Ru atoms, as in the case of biferrocene-$2HgCl_2$ adduct.[2]

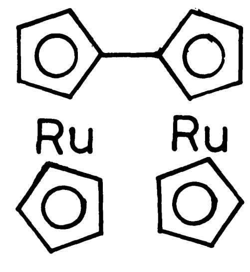
Ferrocenylruthenocene and biruthenocene were prepared by Ullmann coupling of bromoruthenocene and bromoferrocene instead of iodoruthenocene and iodoferrocene.[7,8] The adducts of tin(IV) chloride with ferrocenylruthenocene and biruthenocene were prepared by procedures similar to that described in the case of [2]-ferrocenophane-1.5$SnCl_4$ adduct.[3,4] The products prepared in the reaction of ferrocenylruthenocene and biruthenocene with $SnCl_4$ are so hygroscopic that the elemental analysis and IR spectroscopic data show an appreciable amount of water in each final product, even after keeping the samples in a desiccator. Found: C, 22.36; H, 2.10%. Calcd for ferrocenylruthenocene$(SnCl_4)_{2.5}(H_2O)$, $C_{20}H_{20}FeRuSn_{2.5}Cl_{10}O$: C, 22.14; H, 1.86%. Found: C, 17.01; H, 1.64%. Calcd for biruthenocene$(SnCl_4)_{3.5}(H_2O)$, $C_{20}H_{20}Ru_2Sn_{3.5}Cl_{14}O$: C, 17.28; H, 1.45%.

^{57}Fe-Moessbauer spectroscopic measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode, while ^{119}Sn-Moessbauer spectra were measured against a $Ca^{119m}SnO_3$ source. The I. S. value 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 I. S. and Q. S. values was estimated within 0.02 mm s^{-1}.

Ferrocenylruthenocene reacts with $SnCl_4$ giving black precipitates, of which color is similar to that of a monooxidized salt, ferrocenylferricinium salt. ^{57}Fe- and ^{119}Sn-Moessbauer spectra of the product are shown in Figs. 1 and 2, respectively. The Q. S. value of the adduct in the ^{57}Fe-Moessbauer spectrum at 78 K is 2.25 mm s^{-1}, which corresponds to that of ferrocenylruthenocene



Ferrocenylruthenocene



Biruthenocene

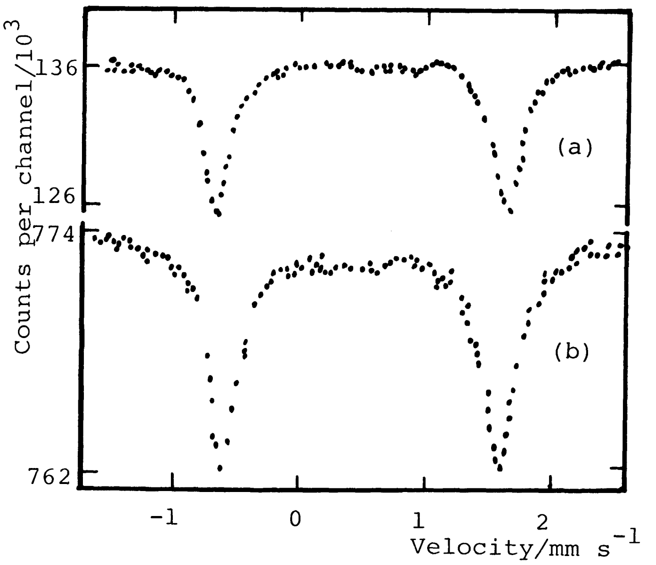


Fig. 1. ^{57}Fe-Moessbauer spectra of (a) ferrocenylruthenocene and (b) its $SnCl_4$ adduct, both at 78 K.

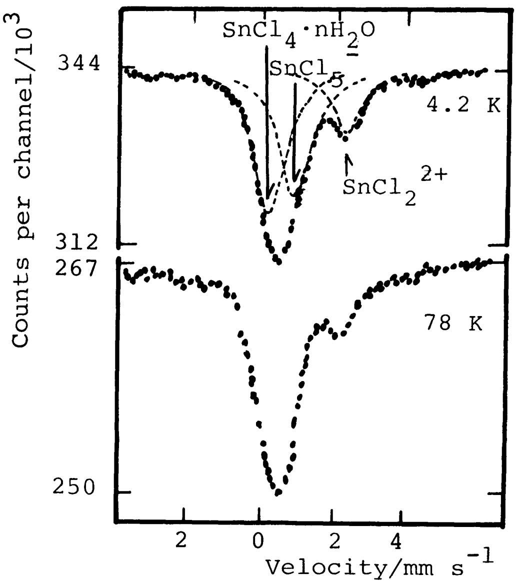


Fig. 2. ^{119}Sn-Moessbauer spectra of ferrocenylruthenocene-$SnCl_4$ adduct at the indicated temperatures.

(2.36 mm s^{-1} at 78 K). The absence of either a broad ferricinium-like singlet line or an anomalously larger quadrupole split line shows that the iron atom in ferrocenylruthenocene is neither oxidized by SnCl$_4$ nor bonded with a Sn(IV) atom like the [2]ferrocenophane-1.5SnCl$_4$ adduct.3) Magnetic susceptibility measurements show that the adduct is diamagnetic from 78 K to 300 K, and this fact is in accordance with the results of ^{57}Fe-Moessbauer spectroscopy.

Although biferrocene is oxidized by SnCl$_4$ giving a paramagnetic monooxidized salt, ferrocenylferricinium salt, the iron atom in ferrocenylruthenocene does not react with SnCl$_4$. Therefore, the ruthenium atom in ferrocenylruthenocene is expected to ligate to SnCl$_4$, because ruthenium atoms in ruthenocene derivatives have e_{2g} electrons softer than those of iron atoms in ferrocene derivatives.

In the ^{119}Sn-Moessbauer spectra of the adduct (shown in Fig. 2), three kinds of chemical states of tin(IV) species (I. S., 0.10, 0.87, and 2.22 mm s^{-1} at 4.2 K and 0.04, 0.71, and 2.14 mm s^{-1} at 78 K) are observed. The component with a higher I. S. value (2.1-2.2 mm s^{-1}) was ascribed to an organotin(IV)-type species and another broad component with lower I. S. values (0.0-0.1 and 0.7-0.9 mm s^{-1}) to inorganic tin(IV) species, $SnCl_4 \cdot nH_2O$ and $SnCl_5^-$, respectively, as already verified in the SnCl$_4$ adducts of [2]ferrocenophane and ruthenocene.4)

Based on the assumption that the recoil-free fraction of the atoms becomes approximately equal at a lower temperature (4.2 K), the areal intensity of the lower I. S. component is estimated to be about four times larger than that of the higher I. S. component. Therefore, it is concluded that ferrocenylruthencene reacts with SnCl$_4$ giving an adduct containing a chemical bond between Ru-Sn atoms, and the adduct is expressed as $[Fe(C_5H_5)(C_5H_4)_2(C_5H_5)Ru\text{-}SnCl_2\text{-}Ru(C_5H_5)(C_5H_4)_2(C_5H_5)Fe]^{2+}\text{-}(SnCl_5^-)_2(SnCl_4)_2(H_2O)_2$, in accord with the elemental analysis data.

However, the adduct is not very stable, that is, on standing at room temperature for several days, the adduct turns into paramagnetic and the intensity of the Sn(II) component in the ^{119}Sn-Moessbauer spectrum increases, suggesting that ferrocenylruthenocene is gradually oxidized by Sn(IV) in solid.

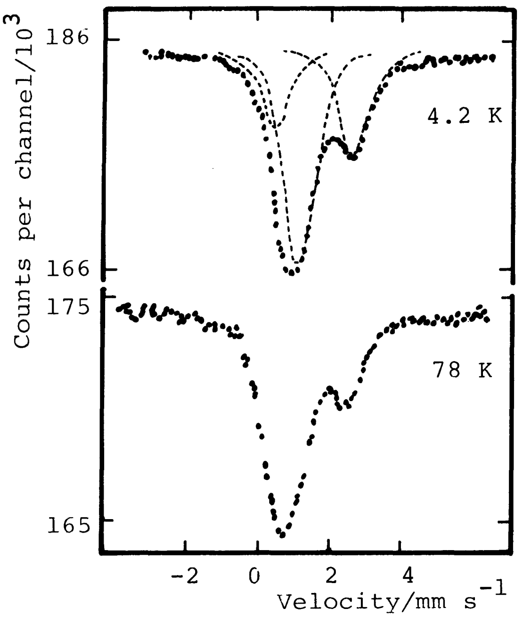
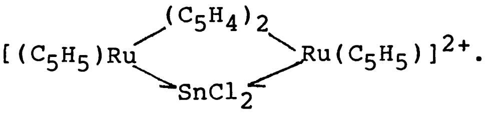


Fig. 3. ^{119}Sn-Moessbauer spectra of biruthenocene-SnCl$_4$ adduct at the indicated temperatures.

Biruthenocene reacts with SnCl$_4$ in a mixture of dried hexane and benzene to give a diamagnetic orange-yellow adduct. The adduct is stable for more than 2 months at room temperature, while ruthenocene-1.5SnCl$_4$ is not as stable as biruthenocene-3.5SnCl$_4$ adduct.

^{119}Sn-Moessbauer spectra of the adduct are shown in Fig. 3. The spectral shape is similar to that of the ferrocenylruthenocene-2.5SnCl$_4$ adduct, and there are three types of tin species (I. S., 0.08, 0.81, and 2.08 at 4.2 K, and 0.04, 0.75, and 2.12 mm s^{-1} at 78 K). By analogy to the ferrocenylruthenocene-2.5$SnCl_4$, the component with a higher I. S. value is ascribable to a Sn-Ru tin(IV) type species and another broad component with lower I. S. values to inorganic tin(IV) species such as $SnCl_4 \cdot nH_2O$ and $SnCl_5^-$. The areal intensity of the lower I. S. components is about 2.5 times larger than that of the higher I. S. component at 4.2 K. Therefore, the adduct is expressed as $[(C_5H_5)(C_5H_4)Ru\text{-}SnCl_2\text{-}Ru(C_5H_4)(C_5H_5)]^{2+}(SnCl_5^-)_2(SnCl_4 \cdot 2H_2O)_{0.5}$, which is in good agreement with elemental analysis data.

Figure 4 shows electronic absorption spectra of the $SnCl_4$ adducts of ruthenocene (upper) and biruthenocene (lower) dissolved in CH_3CN. A new absorption band appears at 27700 cm^{-1} in ruthenocene-1.5$SnCl_4$ adduct, although the intensity of the band decreases rapidly as the solution is allowed to stand for a few minutes after the preparation, probably because of dissociation of the adduct. Although similar dissociation occurs in biruthenocene-3.5$SnCl_4$, the rate is found much smaller, as shown in Fig. 4. The fact that biruthenocene can provide a more stable adduct with $SnCl_4$ than either ferrocenylruthenocene or ruthenocene suggests the possibility of chelation,



$$[(C_5H_5)\mathrm{Ru}\begin{smallmatrix}(C_5H_4)_2\\ SnCl_2\end{smallmatrix}\mathrm{Ru}(C_5H_5)]^{2+}.$$

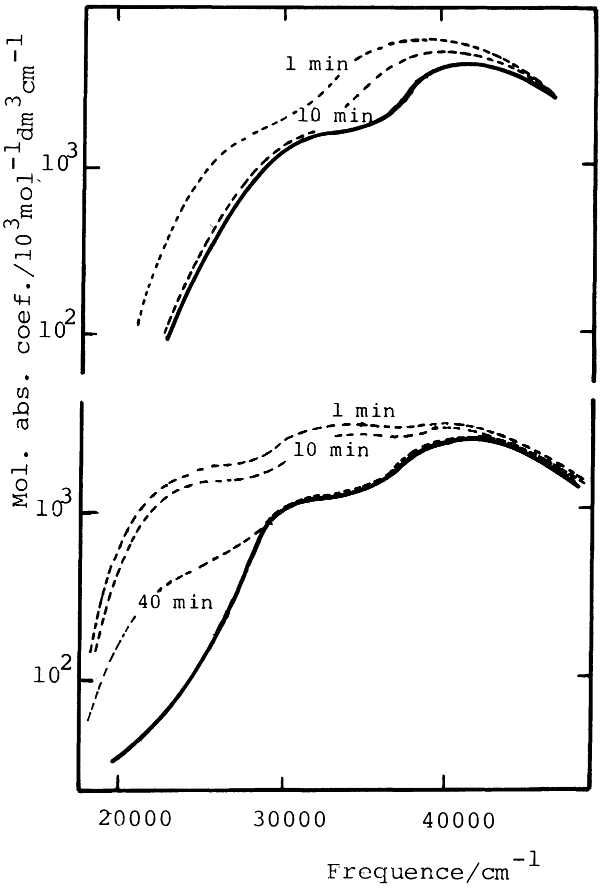


Fig. 4. Absorption spectra of an acetonitrile solution. Upper, (--) ruthenocene and (--) ruthenocene-$SnCl_4$ adduct. Lower, (--) biruthenocene and (--) biruthenocene-$SnCl_4$ adduct at the indicated time after the preparation.

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