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Synthesis and Some Properties of the Complexes of Trithia- and Tetrathia[n](1,1')-ferrocenophanes with $Cu(BF_4)_2$. Intramolecular Redox Reaction in the Complexes

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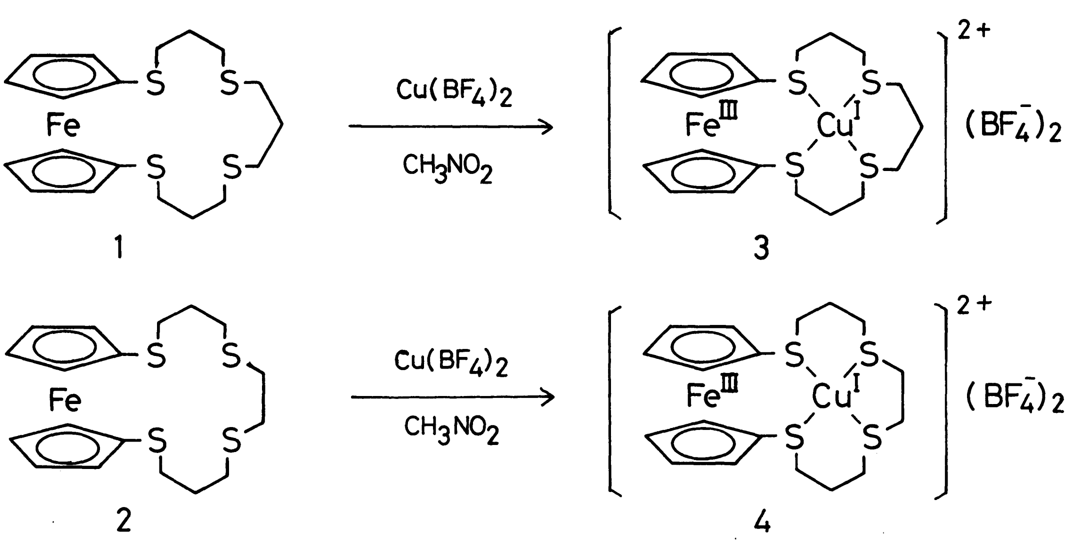
The complexes of 1,5,8,12-tetrathia[12]-, 1,5,9,13-tetrathia[13]-, and 1,5,9-trithia[9](1,1')ferrocenophanes with $Cu(BF_4)_2$ were synthesized. In these complexes, the ferrocene nucleus was oxidized to a cationic ferricenium state and the Cu atom incorporated in the thiamacrocycle was reduced to a Cu(I) state.

Heterobimetallic complexes are possible to aquire unique chemical character or certain stabilization by an unusual coordination manner.[1)] Ferrocene derivatives having electron-donor substituents at the 1,1'-positions are useful organometallic ligands to prepare the heterobimetallic complexes, which are used as the catalyst for hydrogenation of olefins[2)] and for cross-coupling of the Grignard reagents.[3)] Ferrocenocrown ether[4,5)] and ferrocenothiacrown ether[6)] also may well serve for the same purpose. Some metal complexes of the ferrocenocrown[5)] and -thiacrown ethers[7,8)] were reported. We here report the synthesis of the complexes of trithia- and tetrathia[n]ferrocenophanes with copper(II) tetrafluoroborate.

1,5,9,13-Tetrathia[13](1,1')ferrocenophane (**1**) was treated with copper(II) tetrafluoroborate hydrate in ethanol not to give the containing complex (**3**) but

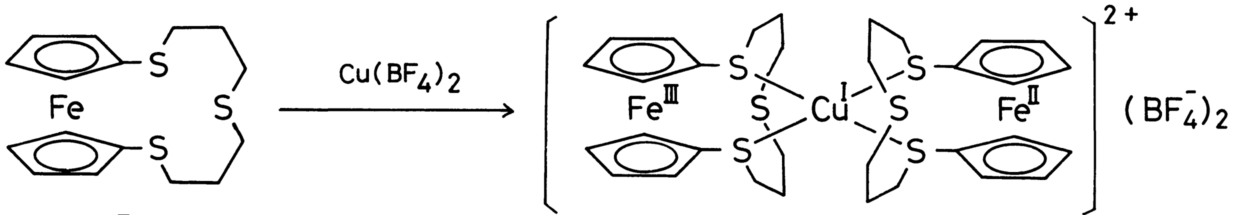


1 3

2 4

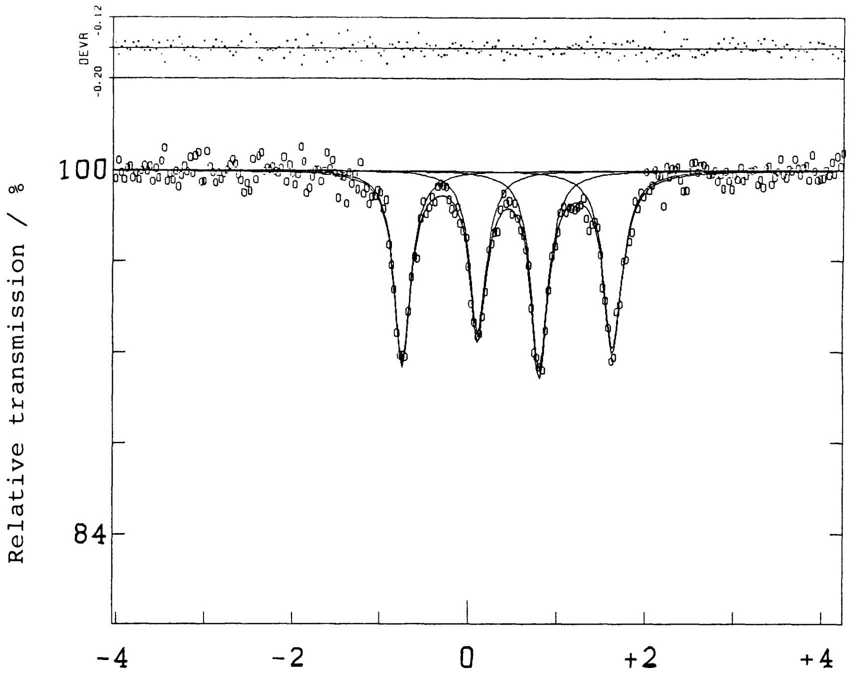
to give the corresponding ferricenium cation (**5**)9) as black needles in good yield. The structure of **5** was identified by its IR and UV-VS spectra superimposable with those of the standard sample which was prepared by oxidation of **1** with benzoquinone and boron trifluoride etherate. When a solution of **1** in nitromethane was mixed with a solution of copper(II) tetrafluoroborate hydrate and acetic anhydride in nitromethane under nitrogen and subsequently diluted with anhydrous ether, black fine needles (mp $\approx$218 °C (dec.)) were isolated in 68% yield, which were confirmed by elemental analysis to be the 1:1 complex (**3**)9) of **1** with $Cu(BF_4)_2$. In a similar manner, the 1:1 complex (**4**)9) of 1,5,8,12-tetrathia[12](1,1')ferrocenophane (**2**) with $Cu(BF_4)_2$ was obtained as black needles in 70% yield. When **3** and **4** were recrystallized from acetonitrile, the corresponding ferricenium cations (**5** and **6**)9) were isolated as black plates in good yields, respectively.

The IR spectrum of the 1:1 complex (**3**) was approximately similar to that of the cation (**5**), although different in details. The absorption assigned to an unsymmetric metal-ligand stretching transition, which appeared at 486 cm^{-1} in the free ligand **1** was shifted to 416 cm^{-1} in **3** and 418 cm^{-1} in **5**, respectively. Oxidation of ferrocene to ferricenium cation is reported to let the corresponding absorption band shift from 478 cm^{-1} to 405-423 cm^{-1}.10) The C-H out of bending vibration, which is observed at 815 cm^{-1} for ferrocene, appears to be the most diagnostic of the oxidation state of ferrocene.11) For example, this absorption band in ferrocenium triiodide was found at 851 cm^{-1}. In the free ligand **1** and its cation **5**, those bands were observed at 816 and 846 cm^{-1}, respectively. The complex **3** showed this absorption at 848 cm^{-1}. In the [0.0]ferrocenophane12) and [2.2]-ferrocenophane-1,13-diyne13) in which the d-electron on the iron atom of the ferrocene nucleus is delocalized in the time scale of IR measurement, the corresponding band apperared at 835 and 842, and 831 cm^{-1}, respectively. Therefore, the positive charge in the complex **3** is suggested to be localized on the iron atom of the ferrocene nulceus. The electronic spectrum of **3** showed the absorption maxima at 295 (log ε 4.14), 340sh (3.93), 455 (3.58), 764 (3.18), and 856 nm (3.22). The absorption properties of **3** do not differ appreciably from those of the cation **5** throughout the UV and visible regions. The same features were found in the complex **4**. Although each absorption cannot be assigned for the present, it is clear that both **3** and **5** have a very similar electronic structure. No absorption was observed near 390 nm where was found a strong absorption characteristic of the complex of 1,4,8,11-tetrathiacyclotetradecane with $Cu(ClO_4)_2$.14) These facts suggest that in the complex **3** the ferrocene nucleus is oxidized to the ferricenium cation and the copper atom incorporated in the thiamacrocycle moiety is reduced to the copper(I) state. This suggestion seems to be also supported by the fact that the complexes **3** and **4** were recrystallized from acetonitrile to give the cations **5** and **6**,



7

8



Velocity / mm·s^{-1}

Fig. 1. The Mössbauer spectrum of **8**

respectively, since the copper(I) ion has a strong affinity to acetonitrile.[15)]

1,5,9-Trithia[9](1,1')ferrocenophane (**7**) was treated with copper(II) tetrafluoroborate hydrate in ethanol, followed by recrystallization from acetone-hexane, to give a 2:1 complex (**8**)[9)] as black plates in 89% yield. The ligand **7** was oxidized with benzoquinone and boron trifluoride etherate to give the corresponding ferricenium cation (**9**) in good yield. In the IR spectrum of **8**, the C-H out of bending vibration was observed at 820 and 854 cm^{-1}, indicating that the complex **8** may contain both the neutral and the oxidized ferrocene nucleus in the molecule. The electronic spectrum of **8** is nearly superimposable with that of the corresponding ferricenium cation **9**. The result is not incompatible with the suggestion drawn from the IR data, since the intensity of the absorption maximum in the free ligand **7** was about a tenth of that of the cation **9**. The Mössbauer spectrum of **8** (Figure 1) provided a confirmative evidence for the suggestion. The quadrupole splitting parameters (QS) of 2.38 and 0.70 mm/s were observed in the complex **8**, indicating the presence of two kind of the iron nuclei in the molecule. The former value is similar to that (2.36 mm/s) of the free ligand **7** and the latter is nearly consistent with that (0.65 mm/s) of the cation **9**. These spectral data suggest that one of the two ferrocene nuclei in the complex **8** is oxidized to a cationic ferricenium state and that the copper atom coordinated to the sulfur atoms exists as the copper(I) state.

The question whether such an intramolecular redox reaction takes place before or after the complex formation remains unexplained. The CV measurement of the complex of **7** with copper(I) perchlorate[8)] in acetonitrile showed only an irreversible wave concerning the redox reaction of the copper atom, suggesting the instability of the Cu(II) complex of **7**. It seems reasonable to suppose that the redox reaction may occur in the stage of a partial coordination of the copper(II) atom to a part of the thiamacrocycle (probably the two sulfur atoms connected directly to the ferrocene nucleus). In the present copper complexes **3**, **4**, and **8**, the irreversible one-electron transfer from the iron atom in the ferrocene nucleus to the copper atom takes place probably in an intramolecular manner, while the reversible electron transfer changes biferrocene16) and [0,0]ferrocenophane12,17) to the corresponding mixed valence compounds, respectively. The irreversibility in the copper complexes seems to be due to the instability of the complex in which the Cu(II) atom is coordinated to the sulfur atoms of the thiamacrocyle.

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