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A Copper(II) Complex of 1,1′-Diacetylferrocene Bis(thiosemicarbazone)

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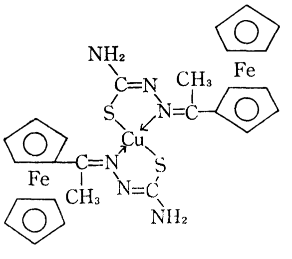
During the course of an investigation of the intramolecular interaction between substituents in 1,1′-disubstituted ferrocenes, we examined the possibility of the intramolecular bridging in complexation of 1,1-diacetylferrocene derivatives. Among many reports on complexes of substituted ferrocenes with inorganic acceptors, there have been a few examples about complexes of 1,1′-disubstituted ferrocenes.[1–4] Hauser and Cain[1] reported a copper(II) complex of 1,1′-dibenzoylacetylferrocene in which cupric ion played a role of an electron acceptor and β-dicarbonyl group played a role of an electron donor. Pavlik and Handlir[2] reported that in the complex of 1,1′-diacetylferrocene with aluminum chloride both carbonyl groups were bound to the monomeric aluminum chloride.

These examples are characteristic to have C=O bonding in donor group. Now we want to report the synthesis and structure of copper complex of 1,1′-diacetylferrocene bis-thiosemicarbazone in which C=N bonding is expected to play a role of a donor.

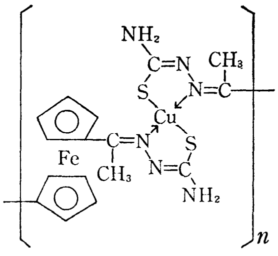
Acetylferrocene thiosemicarbazone (I) and 1,1′-diacetylferrocene bis-thiosemicarbazone (II) were prepared by treatment with thiosemicarbazide. The structure of thiosemicarbazones I and II is in accordance with elemental analyses and the infrared spectra, especially absorptions by N–H stretching vibrations at 3445 to 3150 cm^{-1} and absorptions by C=N group at 1606 cm^{-1} being observed.

The copper(II) complex of acetylferrocene thiosemicarbazone (III) was prepared by treating with cupric acetate. The elemental analysis supports the structure III. In the infrared spectrum of III the intensity of the C=N band at about 1600 cm^{-1} has increased in comparison with that of the corresponding thiosemicarbazone. On the basis of this evidence, it is reasonable to suggest the structure III for the compound.

The copper(II) complex of 1,1′-diacetylferrocene bis-thiosemicarbazone (IV) was prepared in the similar manner as above. From the similarity of the infrared spectrum of this complex IV to that of III, it can be assumed that the structure around cupric ion of this compound is similar to that of III. In order to ascertain this suggestion, the changes of the absorption spectrum of I and II in ethanol by addition of cupric acetate were examined. As shown in Fig. 1, with a decrease in molar ratio of I to cupric acetate, the intensity of the band at 308 nm decreased, while that of the band at 328 nm increased. The absorption spectrum of an equimolar mixture of the thiosemicarbazone and cupric acetate gives a spectrum almost identical with that of III, indicating the formation of the complex III. There is an isosbestic point at 326 nm indicating that only two species, I and III, are present.



(III)



(IV)

The absorption spectra in a series of molar ratio of II to cupric acetate are shown in Fig. 1. The change of absorption spectra with the decrease in molar ratio are very similar to the former case. The absorption spectrum of IV cannot be measured because of its slight solubility, but the absorption spectrum in molar ratio of 1 : 2, in which the formation of the complex appears to be completed, is very close to that of III. These facts also support the structure III and IV.

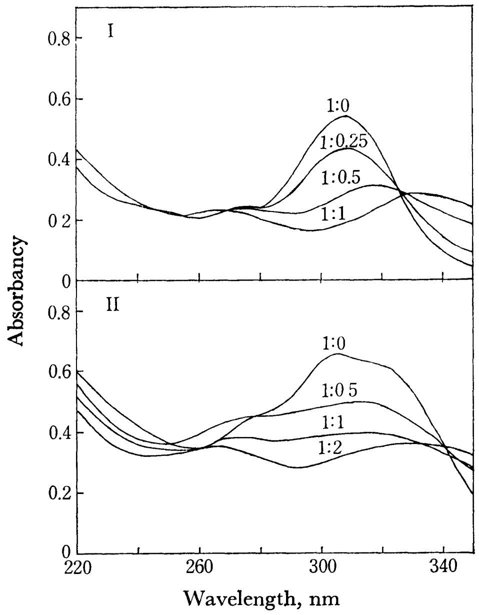


Fig. 1. The changes of the absorption spectra of acetylferrocene thiosemicarbazone(I) and 1,1′-diacetylferrocene thiosemicarbazone(II) upon the addition of cupric acetate. The figures give the molar ratio of thiosemicarbazones (2×10^{-5} mol/l) to cupric acetate.

Experimental

Acetylferrocene Thiosemicarbazone (I). The method for the preparation of copper(II) complex of formylferrocene

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1) C. R. Hauser and C. E. Cain, *J. Org. Chem.*, **23**, 1142 (1958).

2) I. Pavlik and K. Handlir, *Collect. Czech. Chem. Comm.*, **31**, 1958 (1966).

3) I. Pavlik, J. Klikorka, and K. Handlir, *Z. Chem.*, **8**, 390 (1968).

4) E. B. Moynaham, F. D. Popp, and M. F. Werneke, *J. Organometal. Chem.*, **19**, 229 (1969).

thiosemicarbazone[5] was modified and used. Acetylferrocene (5 mmol) in ethanol (20 ml) was added dropwise to a solution of thiosemicarbazide (5 mmol) in water (30 ml). Glacial acetic acid (1 ml) was then added and the resulting mixture was heated in a steam bath for 1.5 hr. After the mixture was cooled the precipitate was collected, washed with aqueous ethanol, dried, and recrystallized repeatedly from ethanol, red crystals, mp 176.5—177.5 °C; yield 43%.

Found: C, 51.73; H, 4.97; N, 14.20%. Calcd for $C_{13}H_{15}FeN_3S$: C, 51.90; H, 5.00; N, 14.00%. IR (KBr) cm^{-1}: 3420, 3285, 3180, 1606, 1591. UV: λ_{max}^{EtOH} nm(ε) 239 (12600), 273 (12400), 308 (27100), 455 (960). NMR (DMSO-d_6): τ 0.10 (s, 1H), 2.00 (bs, 1H), 2.40 (bs, 1H), 5.23 (t, 2H), 5.65 (t, 2H), 5.83 (s, 5H), 7.80 (s, 3H).

1,1′-Diacetylferrocene Bis-thiosemicarbazone (II). In a similar manner as described above, the title compound was prepared and recrystallized repeatedly from ethanol, red crystals, mp 163—164.5 °C; yield 60%.

Found: C, 44.63; H, 5.26; N, 19.27%. Calcd for $C_{16}H_{20}FeN_6S_2$–H_2O: C, 44.25; H, 5.11; N, 19.35%. IR (KBr) cm^{-1}: 3445, 3250, 3150, 1606, 1593. UV: λ_{max}^{EtOH} nm(ε) 280 (22700), 305 (33000), 318 (31300), 458 (1570). NMR (DMSO)-d_6): τ 0.11 (s, 2H), 1.97 (m, 2H), 2.37 (m, 2H), 5.22 (t, 4H), 5.65 (t, 4H), 7.88 (s, 6H).

Copper(II) Complex of Acetylferrocene Thiosemicarbazone (III). Cupric acetate (2.5 mmol) in 25 ml of ethanol was added to a warm solution of acetylferrocene thiosemicarbazone (5 mmol) in 25 ml of ethanol. The resulting mixture was warmed at 70 °C for 1 hr. The precipitate, which formed after cooling, was removed by filtration, washed with aqueous hydrochloric acid solution, water, and cold ethanol, and dried, black powder, mp 160—161 °C; yield 59%.

Found: C, 46.84; H, 4.65; N, 12.05%. Calcd for $C_{26}H_{28}CuFe_2N_6S_2$: C, 47.00; H, 4.20; N, 12.60%. IR (KBr) cm^{-1}: 3465, 3425, 3325, 3200, 3095, 1611, 1598. UV: λ_{max}^{EtOH} nm(ε) 261 (10800), 328 (12000), 431 (1970).

Copper(II) Complex of 1,1′-Diacetylferrocene Bis-thiosemicarbazone (IV). In a similar manner as described above, the copper complex of 1,1′-diacetylferrocene bis-thiosemicarbazone was prepared, brown powder, mp>300 °C; yield 80%. The purification by recrystallization of this copper complex was very difficult because of its slight solubility in most solvents.

Found: C, 39.22; H, 4.02; N, 16.06%. Calcd for $(C_{16}H_{18}CuFeN_6S_2)_n$: C, 40.20; H, 3.77; N, 17.60%. IR (KBr) cm^{-1}: 3440, 3340, 3170, 1614, 1588.

UV Spectra of Copper(II) Complexes of Acetylferrocene Thiosemicarbazone and 1,1′-Diacetylferrocene Bis-thiosemicarbazone. The UV absorption spectra were measured in ethanol. The molar ratio of acetylferrocene thiosemicarbazone and cupric acetate were 1 : 0, 1 : 0.25, 1 : 0.5, and 1 : 1, while those of 1,1′-diacetylferrocene bis-thiosemicarbazone and cupric acetate were 1 : 0, 1 : 0.5, 1 : 1, and 1 : 2.

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[5] D. M. Wiles and T. Suprunchuk, *Can. J. Chem.*, **46**, 1865 (1968).