

Synthesis of heterobimetallic complexes of *N*-ferrocenyl-2-hydroxybenzylideneimine

Mümtaz Ertaş, Vefa Ahsen, Ayşegül Gürek,

*Department of Chemistry, Tübitak-Research Institute for Basic Sciences, P.O. Box 74,
Gebze-Kocaeli (Turkey)*

and Özer Bekâroğlu *

*Department of Chemistry, Technical University of Istanbul, Maslak-Istanbul and Tübitak-Research
Institute for Basic Sciences, P.O. Box 74, Gebze-Kocaeli (Turkey)*

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Abstract

N-Ferrocenyl-2-hydroxybenzylideneimine was prepared by the condensation of ferrocenylamine with salicylaldehyde. Cobalt(II) and zinc(II) complexes of the new ligand were isolated and characterized.

Introduction

In recent years there has been much interest in binuclear complexes. This is partly due to the relevance of binuclear compounds to bioinorganic systems [1], but the main reason lies in the application of binuclear organometallic compounds in catalytic activation of small molecules such as CO [2,3]. Thus model systems have been developed which contain donor sites capable of complexing with two metal ions simultaneously.

We are engaged in a continuing study of the synthesis of binuclear compounds containing ferrocene units and *vic*-dioximes to bind the second metal ion [4–7]. In the case of a [10]ferrocenophane-dioxime, namely 1,10-dithia-4,7-diaza-5,6-bis(hydroxyimino)[10](1,1')ferrocenophane, we observed that the donor properties of the heteroatoms of the phane structure were lowered as a result of interaction with the ferrocene nucleus [7]. We describe here the results of a study of the change in the donor properties of N atoms attached directly to the cyclopentadienyl rings; the Schiff's base of ferrocenylamine with salicylaldehyde has been synthesized, and its complexes with Co^{2+} and Zn^{2+} are described.

Results and discussion

Ferrocenylamine was prepared by Nesmejanov's method [8], in which reaction of bromoferrocene with copper salt of phthalimide gives *N*-ferrocenylphthalimide which is treated with hydrazine to give ferrocenylamine. Condensation reaction of ferrocenylamine with salicylaldehyde gave *N*-ferrocenyl-2-hydroxybenzylideneimine (I) (Fig. 1). This ligand was prepared by Alekseeva et al. [9] in an investigation of hydrogen bonding in ferrocene-containing azomethines, but there has been no report on its complexes.

The mass spectrum of I showed a molecular ion at m/e 306 as expected. In the ^1H NMR spectrum of I, the signals from the α and β protons of bound cyclopentadienyl appeared as two well separated singlets at δ 4.55 and 4.22 ppm, and those of free cyclopentadienyl as a singlet at δ 4.16 ppm. The deuterium-exchangeable OH proton of the salicylidene group appeared at low field (δ 13.4 ppm), which is consistent with the formation of a hydrogen bridge between O—H and the N atom of the azomethine group. This hydrogen bonding was confirmed by the observation of a broad band at $2900\text{--}2700\text{ cm}^{-1}$ in the IR spectrum [10].

Reaction of I with zinc acetate or cobalt acetate was performed in ethanol. The solution gradually became dark-red on addition of a solution of I to the solution of the metal salt. Crystallization of the complexes II and III was complete in about 2 h. Elemental analysis data indicated a 1/2 metal/I ratio (Fig. 2).

The ^1H NMR spectrum of the diamagnetic II was very similar to that of I, lacking only the OH chemical shift, which disappeared after complex formation. In general complexes II and III exhibited very similar IR features, which is indirect evidence that their structures must be the same.

The absorption band corresponding to the *d-d* transition of ferrocene appeared at longer wavelength (475 nm) for I than that for the ferrocene itself (440 nm) [11]. A further bathochromic shift occurred after complexation with Zn (488 nm) or Co (490 nm). This can be accounted for in terms of σ - π conjugation between the Fe—C σ bond of the ferrocene nucleus and the lone pair of the heteroatom (N in this case), as suggested for 1,*n*-dithiaferrocenophanes by Sato et al. [12,13]. In the case of I, the absorption band of ferrocene is shifted to longer wavelength owing to conjugation with C=N π bond and the lone pair of electrons on N atom, but as a result of hydrogen-bonding the lone pair is partially bound. After complex formation the lone pair of electrons forms a N—Metal σ -bond, and back-donation introduces π -bonding. Consequently, a two-way conjugation, which might cause a further

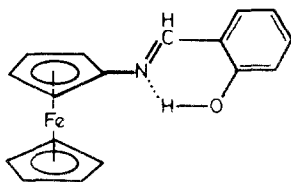


Fig. 1

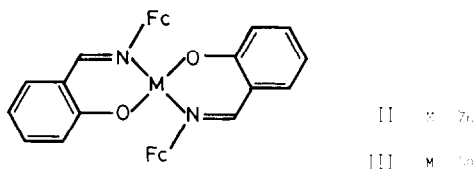


Fig. 2

bathochromic shift, is probable for ferrocene. Studies of the interaction of the ferrocene nucleus with heteroatoms are being continued.

Experimental

Ferrocenylamine was prepared as described previously [8]. ^1H NMR spectra were taken by Bruker AC-200 FT-NMR spectrometer in Tübitak Research Institute for Basic Sciences, Gebze, Turkey.

N-Ferrocenyl-2-hydroxybenzylideneimine (I)

A solution of salicylaldehyde (0.243 g, 2.0 mmol) in 30 ml of ethanol was added dropwise to a solution of ferrocenylamine (0.40 g, 2.0 mmol) in 100 ml of ethanol at room temperature. The mixture was stirred for 1 h, and its colour gradually turned to red before precipitation started. The red crystals were filtered off, washed with ethanol and dried under vacuum. Yield: 0.464 g (76%), m.p. 146 °C. The product was soluble in chloroform, dichloromethane and diethyl ether. ^1H NMR (CDCl_3): δ 4.16(s, 5H), 4.22(s, 2H), 4.55(s, 2H), 6.95(m, 2H), 7.30(m, 2H), 8.6(s, 1H), 13.4(s, 1H, OH) ppm. IR(KBr): 3420, 3100, 3060, 2980, 2920, 2720, 1605, 1570, 1500, 1470, 1410, 1360, 1280, 1200, 1110, 960, 930, 820, 760, 490 cm^{-1} . UV-vis(CH_2Cl_2): λ 475 (ϵ 1860), 392(2300), 336(10300), 308(10760), 260(11060), 230(15940) nm. Analysis. Found: C, 65.75; H, 4.86; N, 4.08. $\text{C}_{17}\text{H}_{15}\text{NOFe}$ calc.: C, 66.91; H, 4.95; N, 4.59%.

Bis(N-ferrocenyl-2-hydroxybenzylideneiminato)zinc (II)

A solution of I (0.3 g, 1 mmol) in 50 ml of ethanol was added to a solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.11 g, 0.5 mmol) in a mixture of water/ethanol (25 ml). The mixture was stirred at 70 °C for 2 h and then evaporated under vacuum. The residue was washed with ethanol and dried. Yield: 189 mg (56%), m.p. 264 °C. ^1H NMR (CDCl_3): δ 4.15(s, 10H), 4.23(s, 4H), 4.60(s, 4H), 6.80(t, 2H), 6.97(d, 2H), 7.24(d, 2H), 7.38(t, 2H), 8.62(s, 2H) ppm. IR (KBr): 3100, 3010, 2940, 1600, 1585, 1530, 1450, 1410, 1385, 1340, 1320, 1280, 1230, 1190, 1150, 1100, 1045, 1000, 940, 905, 810, 750, 590, 500 cm^{-1} . UV-vis (CH_2Cl_2): λ 488 (ϵ 4720), 398(10920), 347 sh(12400), 305(22480), 248 sh(22000), 230(33200) nm. Analysis. Found: C, 60.47; H, 4.28; N, 4.05. $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_2\text{Fe}_2\text{Zn}$ calc.: C, 60.62; H, 4.19; N, 4.16%.

Bis(N-ferrocenyl-2-hydroxy-benzylideneiminato)cobalt (III)

A solution of I (0.305 g, 1 mmol) in 50 ml of ethanol was added to a solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.125 g, 0.5 mmol) in 20 ml of ethanol. The mixture was stirred under reflux for 2 h. The purplish-dark red crystals which separated were filtered off, washed with ethanol and then with diethyl ether, and dried under vacuum. Yield: 190 mg, (52%); m.p. 275 °C.

IR (KBr): 3100, 3015, 2920, 1600, 1575, 1530, 1450, 1410, 1380, 1340, 1315, 1275, 1220, 1185, 1150, 1100, 1030, 1000, 940, 910, 810, 760, 600, 500 cm^{-1} . UV-vis (CH_2Cl_2): λ 490(ϵ 4240), 390(10320), 345(17320), 304(20520), 230(30720) nm. Analysis. Found: C, 60.89; H, 4.21; N, 4.47. $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_2\text{Fe}_3\text{Co}$ calc.: C, 61.20; H, 4.23; N, 4.20%.

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References

- 1 D. Coucouvanis, *Acc. Chem. Res.*, 14 (1981) 201.
- 2 C.P. Casey, R.F. Jordan and A.L. Rheingold, *J. Am. Chem. Soc.*, 105 (1983) 665.
- 3 G.S. White and D.W. Stephan, *Inorg. Chem.*, 24 (1985) 1499.
- 4 M. Ertaş, A.R. Koray, V. Ahsen and Ö. Bekâroğlu, *J. Organomet. Chem.*, 317 (1986) 301.
- 5 M. Ertaş, A.R. Koray, V. Ahsen and Ö. Bekâroğlu, *J. Organomet. Chem.*, 319 (1987) 197.
- 6 M. Ertaş, V. Ahsen, A. Gül, and Ö. Bekâroğlu, 333 (1987) 383.
- 7 M. Ertaş, V. Ahsen, A. Gül, and Ö. Bekâroğlu, 335 (1987) 105.
- 8 A.N. Nesmejanow, W.A. Ssusonowa, and V.N. Drosd, *Chem. Ber.*, 93 (1960) 2717.
- 9 I.A. Alekseeva, G.N. Yashchenko, T.A. Sinitsyna, and L.A. Petrov, *Zh. Obshch. Khim.*, 47 (1977) 1874 (*J. Gen. Chem. USSR*, 47 (1977) 1712).
- 10 V. Ahsen and Ö. Bekâroğlu, *Synth. React. Inorg. Met. Org. Chem.*, 15 (1985) 61.
- 11 K.I. Grandberg, S.P. Gubin, and E.G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1966) 549.
- 12 M. Sato, S. Tanaka, S. Ebine, and S. Akabori, *Bull. Chem. Soc. Jpn.*, 57 (1984) 1929.
- 13 M. Sato, S. Tanaka, S. Ebine, K. Morinaga, and S. Akabori, *J. Organomet. Chem.*, 282 (1985) 247.