Synthesis of ferricinium bis[π-(3)-1,2-dicarbollyl]cobaltate(III), $[Fe^{III}(\eta^5-Cp)_2]^+\{Co^{III}[\pi-(3)-1,2-B_9C_2H_{11}]_2\}^-$

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Ferricinium bis[π-(3)-1,2-dicarbollyl]cobaltate(III), $[Fe^{III}(\eta^5-\pi-Cp)_2]^+\{Co^{III}[\pi-(3)-1,2-B_9C_2H_{11}]_2\}^-$, has been prepared by the reaction of $Fe^{III}(\eta^5-\pi-Cp)_2^+$ with the anion $\{Co^{III}[\pi-(3)-1,2-B_9C_2H_{11}]_2\}^-$. It is a light-green amorphous precipitate that is stable as a dry solid up to 227 °C and unstable in solutions of acetonitrile and acetone.

Key words: dicarbollylcobalt(III); ferricinium salts.

Salt-like derivatives of the ferricinium cation, $Fe^{III}Cp_2^+$, with bulky anions such as $GaCl_4^-$, $Cr(NH_3)_2(SCN)_4^-$, $C_6H_2N_3O_7^-$, *etc.*, some prepared by precipitation from aqueous media,[2] are known.[1,2] Cluster anionic derivatives of boranes and carboranes are well known; many of these compounds can act in principle as precipitating agents for $Fe^{III}Cp_2^+$ and its analogs with other metals to form the corresponding salts and complexes. Therefore, a wide range of compounds may exist in which cluster borane anions combine with metallocenium cations and their derivatives. The literature data on these compounds are scarce. In particular, salt-like $CoCp_2^+$ complexes with anionic metal derivatives of carboranes of the sandwich type, $[Co(B_9C_2H_{11})_2]^-$ and $[Co(B_8C_2H_{10})_2]^-$, which were prepared in organic media as intermediates in the synthesis of more complex cobalt-carborane clusters have been reported.[3,4] We found no data on compounds of this type containing $Fe^{III}Cp_2^+$ (the classic representative of metallocenium compounds).

We synthesized a salt-like compound of the $Fe^{III}Cp_2^+$ cation with the $\{Co^{III}[\pi-(3)-1,2-B_9C_2H_{11}]_2\}^-$ anion (**1**) by precipitation in a weakly acidic medium. Anion **1** is a metal derivative of *ortho*-carborane, in which the cobalt(III) atom is in the π-sandwich position.[5,6]

When the conditions for the synthesis of the complex under consideration are determined, account must be taken of the fact that the reduction of $Fe^{III}Cp_2^+$ to ferrocene[1,2] in aqueous media starts at pH > 2. On the other hand, in a strongly acidic medium, decomposition, protonation, and hydrolysis of anion **1** are possible. Anion **1** is also a carrier of hydride hydrogen, which is a strong reducer, and the reduction of $Fe^{III}Cp_2^+$ is possible.

Taking into account these features, compound $[Fe^{III}(\eta^5-\pi-Cp)_2]^+\{Co^{III}[\pi-(3)-1,2-B_9C_2H_{11}]_2\}^-$ (**2**) was synthesized in a minimally acidic aqueous buffer medium at pH ~4.6 as rapidly as possible without heating the reaction mixture.

Experimental

IR spectra were recorded on a UR-20 instrument using KBr pellets.

Synthesis of ferricinium bis[π-(3)-1,2-dicarbollyl]cobaltate(III) (2). A cesium salt of anion **1** prepared and characterized according to the procedure reported previously was used.[5,6] The $Fe^{III}Cp_2^+$ cation in an aqueous hydrochloric acid solution was prepared by stirring a benzene solution of ferrocene with an aqueous solution of $FeCl_3$ adjusted to pH ~1.5 with HCl. To prepare complex **2**, a hot aqueous solution of the cesium salt of anion **1** (2.01 g) and a $Fe^{III}Cp_2^+Cl^-$ solution (a stoichiometric excess of 15 %) were introduced simultaneously dropwise into a flask containing 300 mL of an acetate buffer solution with pH 4.6 at 25 °C with active stirring. By this means the possibility of rapid reduction, decomposition, and protonation of components was eliminated. Under these conditions, complex **2** was formed as a flocculent amorphous solid pale-green precipitate. The obtained precipitate was quickly isolated from the mother liquor by centrifugation in a high-speed refrigerated centrifuge with a cooled rotor; the precipitate was washed with diluted MeCOOH and water until the washing liquids were completely decolorized, and then the precipitate was dried *in vacuo* at 70 °C to constant weight. The yield of complex **2** was 2.11 g (83.2 % with respect to **1**). Found (%): Co, 11.17; Fe, 10.68; B, 36.01; $[Co(B_9C_2H_{11})_2]^-$, 64.70. $[Fe(C_5H_5)_2]^+[Co(B_9C_2H_{11})_2]^-$. Calculated (%): Co, 11.55; Fe, 10.96; B, 38.20; $[Co(B_9C_2H_{11})_2]^-$, 63.51.

IR spectrum of **2**, ν/cm^{-1}: 3106 m (C—H of ferricinium, according to Ref. 2); 2512 shoulder, 2527 s, 2562 s, 2599 shoulder, 2610 shoulder (B—H in $B_9C_2H_{11}^{2-}$, according to Ref. 6); 3028 m, 3045 m (C—H in $B_9C_2H_{11}^{2-}$).

Properties of complex 2. The DTA curve coupled with the curve of gas evolution for complex **2** at 227 °C shows an endothermic effect, immediately followed by an exothermic effect occurring with gas evolution, frothing, and darkening of

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the weighed sample and also with sublimation of ferrocene, which condensed on the cold part of the ampule. Therefore, when complex **2** is subjected to thermolysis, it decomposes, and $Fe^{III}Cp_2^+$ is reduced to ferrocene. Compound **2** is rapidly decomposed with an aqueous Na_2SO_3 solution to give a ferrocene precipitate, whereas anion **1** is quantitatively transferred to the aqueous phase. Compound **2** is soluble in $(MeCO)_2O$; however, when slowly evaporated, the obtained dark-blue solution yields an amorphous precipitate. Compound **2** dissolves in acetone and acetonitrile to afford intensely blue solutions; this color is typical of the $Fe^{III}Cp_2^+$ cation. However, the liquids develop a bright-yellow color after several minutes. This hinders the study of complex **2** by such methods as NMR spectroscopy and X-ray diffraction analysis (it is impossible to obtain single crystals). We failed to record Raman spectra of solid **2** using excited He—Ne light and an argon ion laser because the compound changes under light.

Results and Discussion

It was established that the $Fe^{III}Cp_2^+$ cation readily precipitates in a weakly acidic medium in the form of compound **2** when treated with the cesium salt of anion **1**. As a result, we obtained salt-like compound **2**, in which two different-type components (containing Fe^{III} and Co^{III}) of the π-sandwich structure are present as a cation and an anion. Hence, the range of compounds of cations of the type $M(\pi\text{-}Cp_2)^+$ with anionic borane clusters is extended. Compound **2** is fairly stable under the conditions of the synthesis and when stored in air, but it irreversibly decomposes at 227 °C and rapidly changes in acetone and acetonitrile solutions. Apparently, in this case, the inherent instability of the type **2** system, in which a readily reduced ferricinium cation combines with anion **1**, a carrier of hydride hydrogen shows up. The susceptibility of ferricinium to reduction in the solid phase of **2** is hindered at moderate temperatures but reduction can readily occur in organic solutions and on heating.

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