Letters to the Editor

A binuclear iron(III) complex of a new tridentate binucleating ligand, 2-(2,2′-bipyrid-6-yl)methoxybenzoic acid

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There is interest in the synthesis of binuclear iron μ-oxo complexes because they are significant for modeling methanemonoxygenase (MMO).[1] Since similar complexes with simple ligands[2] are insufficiently stable in catalytic or redox processes, there have been attempts to increase their stability by binding simple ligands to framework type polydentate ligands (usually including a bridged oxygen atom as an alkoxide or phenoxide group, $-O^-$). The design of this approach is similar to that used by nature for creating nonheme iron-containing enzymes in which enzymatic amino acid residues bound to a polypeptide framework form an active center of the enzyme during complex formation with iron. However, the bridged oxygen atom in MMO is not bound to the polypeptide framework, but it is formed by an exogenic water molecule. Therefore, to design an adequate model of MMO, it is reasonable to bind a bridged carboxylate group to the terminal ligand group. Evidently, this problem is not simple, because there have been at least two unsuccessful attempts to synthesize similar complexes.[3,4]

In this work, we report on the synthesis of a new chelate tridentate ligand 2-(2,2′-bipyrid-6-yl)methoxybenzoic acid, BPBA (**1**, R = H), containing a bipyridyl group and a carboxylate function bound in such a way that, when iron(III) forms a complex with this ligand, the carboxylate group retains its capability of functioning as an additional bridge in the binuclear μ-oxo complex. In fact, we were able to isolate and characterize the first complex of this type, $[Fe_2O(BPBA)_2(H_2O)_2](ClO_4)_2$ (**2**). Our preliminary studies indicate that it is highly stable (more detailed data will be published elsewhere).

Ligand **1** was obtained from bipyridyl by a five-stage synthesis (Scheme 1) in a total yield of 30% and was characterized by elemental analysis and ^1H NMR and IR spectroscopic data.

Compound **1** (R = H), IR (KBr), ν/cm^{-1}: 3450 (OH); 3000, 3100 (bipy); 2480, 2361, 1910, 1686 (C=O); 1601, 1569 (C_6H_4); 1492, 1433 (bipy); 1360, 1300, 1288, 1255, 1137, 1012, 850, 773, 750 (CN, bipy); 667, 636. ^1H NMR (200 MHz, $CDCl_3$, $SiMe_4$ as an internal standard), δ: 8.71 (d, 1 H, H(17)); 8.46 (t, 2 H, H(9), H(6)); 8.25 (q, 1 H, H(11)); 7.91 (m, 2 H, H(4), H(10)); 7.59 (t, 1 H, H(15)); 7.39 (m, 2 H, H(16), H(3)); 7.2 (m, 2 H, H(5), H(14)); 5.45 (s, 2 H, H(7)).

After storage for several days, dark-green crystals of complex **2** precipitate from a solution of equimolar amounts of the sodium salt of **1** and iron(III) perchlorate in a MeCN—MeOH (1.5 : 1.0) mixture diluted with a two-threefold excess of ethanol. According to the elemental analysis data, the composition of the complex is $\mathbf{2} \cdot 4H_2O$. The yield is 80%. For compound **2**, the UV (λ_{max}/nm: 320 sh, 360 sh, 485 and 640), Raman (Fe—O—Fe ν_s 498 and 534 cm^{-1}), and ^1H NMR (22, 18, 15, 12, 9, 7, and 4 ppm) spectra in MeCN are very similar to the corresponding spectra for binuclear iron(III)

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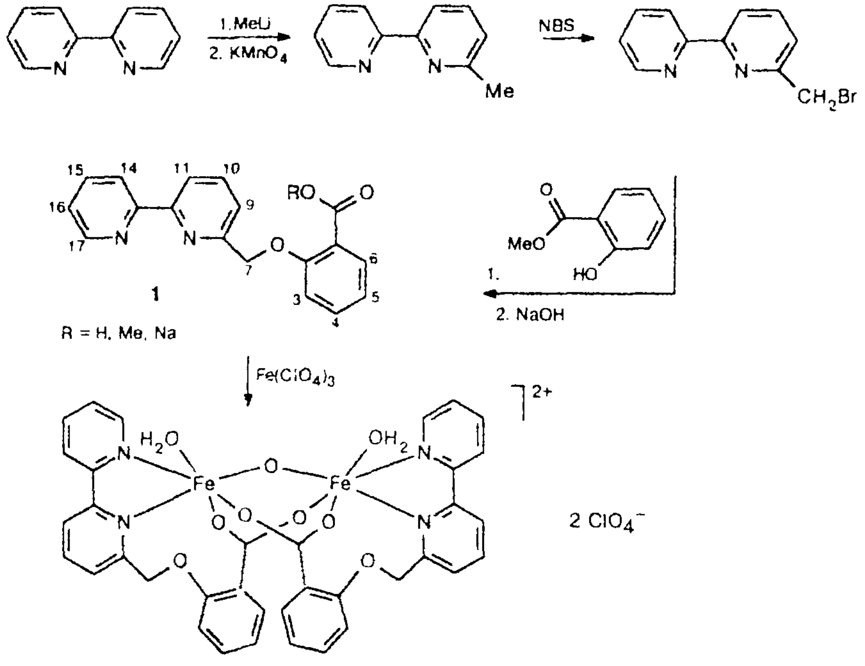
Scheme 1



bridged μ-oxo complexes with similar ligand groups.[2] The difference between the absorption frequencies of the symmetric and asymmetric stretching vibrations of the carboxylate group, $\Delta\nu = \nu_{as} - \nu_s = 204$ cm^{-1}, corresponds to bridge type binding of carboxylate, although it is somewhat higher than the values (110—160 cm^{-1}) usually observed for the majority of iron(III) μ-carboxylate complexes. This is likely caused by the nonequivalence of the Fe—O(carboxylate) bonds due to the rigid structure of the ligand. The binuclear structure of complex **2** is also confirmed by the observation of an ion with a charge of 2+ and a mass of 738 in the mass spectrum (ES) of a 10^{-4} *M* solution of the complex in MeCN, which correspond to the charge and mass of the cation of **2** without water molecules.

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