Synthesis, structure, and properties of a new trinuclear iron cluster, $[(MeOH)(H_2O)_2Fe_3(\mu_3\text{-}O)(\mu\text{-}OOCC_6H_4OCH_2C_5H_4NH)_6](ClO_4)_7 \cdot 8MeOH \cdot 3.5H_2O$

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Reactions of iron(III) salts with a new bidentate ligand, which is potentially capable of forming binuclear iron complexes upon complexation, were studied. Under various conditions, we succeeded in isolating only the trinuclear cationic complex $[Fe^{III}{}_3(O_2CR)_6(\mu_3\text{-}O)]^{7+}$ (**1**), where RCO_2 is 2-(pyrid-2-ylmethoxy)benzoic acid protonated at the pyridyl moiety. The structure of **1** was established by spectral, magnetic, and X-ray structural studies. Cyclic voltammetry in MeCN in the temperature range from −35 to 20 °C demonstrated that **1** undergoes successive $Fe^{III} \rightarrow Fe^{II}$ reduction in three one-electron stages, which is indicative of the electronic interaction between iron atoms in the complex.

Key words: trinuclear iron carboxylate complexes, synthesis, X-ray structural analysis, spectroscopy, cyclic voltammetry.

Polynuclear μ-oxo-bridged clusters of metals are of interest as objects of studies of magnetic exchange interactions or intramolecular electron transfer, as catalysts for various reactions, and as models of active centers of a number of metalloenzymes. Particular attention has been given to binuclear μ-oxo-bridged complexes of iron because of their similarity to the active centers of a number of important nonheme iron-containing proteins, such as hemerythrin, ribonucleotide reductase, and methane monooxygenase (MMO).[1]

However, the synthesis of these compounds is very difficult because equilibrium is established between mononuclear complexes and clusters with different numbers of nuclei upon hydrolysis of iron salts. Therefore, the possibility of isolating μ-oxo compounds, which have particular structures, depends on many factors, among which are the nature of the solvent, the solubility of the complex, the presence of bases, and the structural and electronic characteristics of ligands.

Previously,[2] the ligands in which the terminal groups are bonded to alkoxo or phenoxo groups capable of bridging two iron atoms were used for the stabilization of the binuclear structure. However, these models are not adequate to the active center of methane monooxygenase and are inconsistent with the hypothesis[3] that the bridging oxygen atom participates in the catalytic process. Therefore, it is of interest to construct basically new ligands of this type in which potentially terminal groups are bonded to the carboxylate bridge formed. Apparently, this is a difficult task because at least one unsuccessful attempt to realize this idea was reported recently.[4]

As part of our systematic studies aimed at preparing new ligands for the synthesis of binuclear iron complexes, we constructed a new bidentate ligand, namely, 2-(pyrid-2-ylmethoxy)benzoic acid potentially capable of forming binuclear complexes (Fig. 1). This ligand belongs to the simplest type of complex ligands of this kind in which a potentially bridging carboxylate group is bonded to the terminal monodentate ligand to be formed and can be considered as the base ligand for further evolution with the aim of developing a family of more perfect ligands. As will be seen from the following discussion, the complexing ability of this ligand appeared to be inadequate to stabilize the binuclear structure, and, therefore, we now intend to attach a bidentate terminal group to the carboxylate ligand.

Experimental

2-(Pyrid-2-ylmethoxy)benzoic acid. A solution of picolyl chloride (11.78 g, 93 mmol) and sodium iodide (2.8 g, 18 mmol) in dry acetone (15 mL) was kept with slight cooling for ~14 h. A solution of methyl salycilate (13.5 g, 93 mmol) in acetone (10 mL) and calcined potassium carbonate (14.1 g, 98 mmol) were added to the reaction mixture, and the mixture

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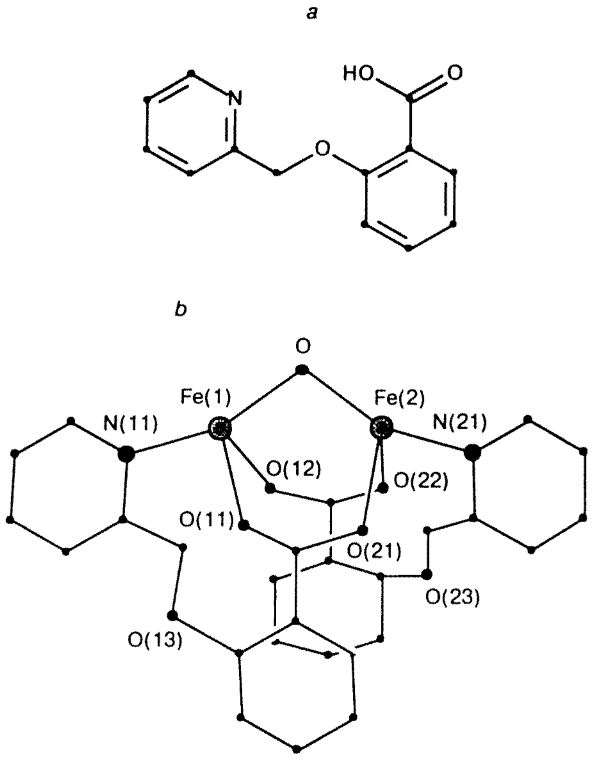

Fig. 1. Structures of the 2-(pyrid-2-ylmethoxy)benzoic acid ligand (*a*) and the computer model of the binuclear complex proposed (*b*).

was refluxed for 10 h using a reflux condenser protected from air moisture with a calcium-chloride tube. The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on a column packed with SiO_2 (Silpearl, 60 mesh) using a 1 : 1 benzene—ethyl acetate mixture as the eluent. The fraction containing the major product was concentrated to dryness and methyl 2-(pyrid-2-ylmethoxy)benzoate was obtained as colorless crystals, m.p. 68 °C. The product was transferred into a 5 % NaOH solution (100 mL) and boiled for 2.5 h until it completely dissolved. Then the solution was cooled with an ice—salt mixture and neutralized with 3 % HCl to pH 6. The precipitate formed was filtered off and recrystallized from 2-propanol. Colorless crystals were obtained in a yield of 14.6 g (69 %), m.p. 153 °C. Found (%): C, 68.02; H, 4.88; N, 6.12. $C_{13}H_{11}NO_3$. Calculated (%): C, 68.12; H, 4.80; N, 6.11. IR (Na 2-(pyrid-2-ylmethoxy)benzoate), ν/cm^{-1}: 1597, 1584, 1573, 1491, 1342, 1312, 1226, 1205, 1170, 1106, 1056, 1038, 849, 801, 766, 731, 676, 625.

Synthesis of the $[(MeOH)(H_2O)_2Fe_3(\mu_3\text{-}O)(\mu\text{-}OOCC_6H_4OCH_2C_5H_4NH)_6](ClO_4)_7 \cdot 8MeOH \cdot 3.5H_2O$ complex (1). A solution of 2-(pyrid-2-ylmethoxy)benzoic acid (1.0 g, 2.12 mmol) in MeOH (10 mL) was treated with NaOH (174 mg, 2.12 mmol). The solution of sodium 2-(pyrid-2-ylmethoxy)benzoate obtained was added dropwise with stirring to a solution of $Fe(ClO_4)_3 \cdot 10H_2O$ (1.13 g, 4.30 mmol) in MeOH (10 mL) for 10 min. The dark-brown solution obtained was kept cooled for several days. The dark orange-red crystals formed were rapidly filtered off on a glass filter; the yield was 1.15 g (60 %). The loss of solvate molecules occurs upon prolonged storage, and an orange finely crystalline powder formed. Found (%): C, 38.71; H, 3.35; N, 3.47; Cl, 10.30; Fe, 6.8. $C_{87}H_{107}Cl_7Fe_3N_6O_{61.5}$. Calculated (%): C, 38.14; H, 3.46; N, 3.42; Cl, 10.10; Fe, 6.82. IR, ν/cm^{-1}: 3392 (OH); 3273, 2500, 1602 ($\nu_{as}COO^-$); 1567, 1532, 1490, 1449, 1402 (ν_sCOO^-); 1283, 1248, 1109 (ClO_4^-); 861, 758 (protonated pyridine); 671, 625 (ClO_4^-); 560.

Magnetic measurements. The magnetic susceptibility of complex **1** was measured on an instrument at the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences[5] using the Faraday method in the temperature range of 296—77 K. The values of the magnetic moments were calculated by the following formula:

$$\mu_{eff} = (8\chi_m T)^{1/2}.$$

The exchange parameters ($-2J$) between paramagnetic iron(III) atoms were calculated using the Heisenberg—Dirac—Van Vlek model[6] with the use of the program package reported previously.[7,8]

Mössbauer spectra were recorded on a standard spectrometer at a constant rate in the zero external field. The Mössbauer parameters were assigned to free metal at ambient temperature. The samples have the natural ^{57}Fe content.

Electrochemical measurements were carried out under an atmosphere of dry argon in MeCN, which had been purified according to the standard procedure.[9] A solution of Bu_4NPF_6 or Bu_4NBF_4 (0.1 *M*), which were preliminarily dehydrated by melting *in vacuo*, was used as the supporting electrolyte. Low-temperature electrochemical measurements were carried out using a cell thermostatically controlled with ethanol, which was cooled with liquid nitrogen in a Dewar vessel. All potentials were measured relative to an aqueous saturated calomel electrode by comparing the potential of the reference electrode (an Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the solution studied by a bridge filled with the supporting electrolyte, with the potential of the redox transition of ferrocene$^{0/+}$ in MeCN (E^0 = 0.42 V, saturated calomel electrode). A 1-mm disk Pt or Au electrode sealed into glass and polished off with diamond paste (the grain size was 1 μm) were used as working electrodes. Cyclic voltammograms were measured using a PAR 173 potentiostat with compensation of ohmic losses and a PAR 175 generator of signals.

X-ray structural analysis. Orange-red crystals of complex **1** are unstable in air at room temperature (apparently, due to the

Table 1. Crystallographic parameters of complex **1**

Space group	$P\bar{1}$
a/Å	15.056(4)
b/Å	17.389(4)
c/Å	23.027(6)
α/deg	107.28(2)
β/deg	94.84(2)
γ/deg	95.71(2)
V/Å^3	5687(3)
Z	2
ρ_{calc}/g cm^{-3}	1.520
Radiation	Mo-Kα (λ = 0.71073 Å)
θ—2θ Scanning range	2—48
Number of measured reflections	13485
Number of reflections with $I > 4.0\sigma$	6585
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0023F^2$
R	0.084
R_w	0.111

loss of solvate molecules), and therefore, the experimental data were collected at −130 °C on a four-circle automated Siemens R3/m diffractometer. Intensities of three standard reflections ($0 < \chi < 65°$) showed no decrease in the course of data collection. Because of a low value of the coefficient (μ = 6.46 cm^{-1}), absorption was ignored. The structure was solved by direct methods. Nonhydrogen atoms of the trinuclear cation and the chlorine atoms of perchlorate anions were refined anisotropically by the full-matrix least-squares method; nonhydrogen atoms of H_2O and MeOH solvate molecules and O atoms of perchlorate anions were refined isotropically. The H atoms in the cation were placed in geometrically calculated positions and these positions were not refined because of the limited number of the reflections measured. All calculations were carried out using the SHELX PLUS program package (the PC version).[10] Crystallographic parameters, the details of structure solution and refinement of **1** are given in Table 1; coordinates of nonhydrogen atoms are listed in Table 2; selected parameters of the trinuclear cation are given in Table 3.

Table 2. Atomic coordinates and equivalent isotropic temperature factors for complex **1**

Atom	*x*	*y*	*z*	B_{eq}
Fe(1)	2472(1)	212(1)	1832(1)	20(1)
Fe(2)	4372(1)	847(1)	2732(1)	21(1)
Fe(3)	2488(1)	656(1)	3335(1)	20(1)
O	3101(6)	561(5)	2627(4)	18(4)
O(1)	1619(6)	−342(5)	2921(4)	26(4)
O(2)	1768(6)	−776(5)	1915(4)	21(4)
O(3)	1159(7)	−2348(5)	1395(4)	40(4)
O(4)	3170(6)	1731(5)	3859(4)	22(4)
O(5)	4430(7)	1851(6)	3425(4)	36(4)
O(6)	2937(7)	3202(5)	4622(4)	34(4)
O(7)	3319(6)	47(5)	3683(4)	26(4)
O(8)	4630(6)	206(6)	3306(4)	32(4)
O(9)	5637(7)	−960(6)	3329(4)	37(4)
O(10)	3373(6)	−493(5)	1403(4)	24(4)
O(11)	4631(6)	−139(5)	2057(4)	31(4)
O(12)	4352(7)	−1884(5)	1926(4)	37(4)
O(13)	1599(6)	1319(5)	3086(4)	30(4)
O(14)	1414(6)	811(5)	2057(4)	26(4)
O(15)	1287(8)	2743(6)	2512(5)	51(5)
O(16)	3016(6)	1167(5)	1595(4)	26(4)
O(17)	4365(6)	1533(5)	2178(4)	24(4)
O(18)	2450(7)	2294(6)	1160(4)	39(5)
O(19)	1814(6)	731(5)	4080(3)	25(4)
O(20)	5777(6)	1103(5)	2826(4)	30(4)
O(21)	1771(6)	−84(5)	954(4)	28(4)
N(1)	2036(10)	−3731(8)	209(6)	56(7)
N(2)	936(8)	4020(7)	5075(6)	39(6)
N(3)	6351(8)	−698(7)	2402(5)	28(5)
N(4)	4000(9)	−2838(7)	3057(6)	41(6)
N(5)	2823(11)	4520(7)	2752(5)	62(7)
N(6)	847(8)	1485(6)	1037(5)	27(5)
C(1)	1444(10)	−854(8)	2378(7)	28(6)
C(2)	756(10)	−1551(8)	2322(6)	22(6)
C(3)	197(11)	−1509(9)	2793(6)	32(7)
C(4)	−467(11)	−2094(9)	2788(7)	36(7)
C(5)	−597(10)	−2797(8)	2301(7)	30(7)
C(6)	−72(11)	−2887(8)	1830(7)	35(7)
C(7)	605(11)	−2272(9)	1846(6)	32(7)
C(8)	1045(12)	−3077(8)	905(7)	43(7)
C(9)	1794(11)	−3035(9)	536(6)	33(7)
C(10)	2218(11)	−2342(11)	496(7)	42(8)
C(11)	2893(12)	−2340(11)	111(7)	49(8)
C(12)	3113(13)	−3104(13)	−213(7)	58(9)
C(13)	2683(14)	−3787(12)	−167(8)	66(10)
C(14)	3941(9)	2078(8)	3848(5)	23(6)
C(15)	4334(12)	2830(8)	4367(6)	27(7)
C(16)	5264(13)	2956(10)	4475(7)	40(7)
C(17)	5738(12)	3596(12)	4949(8)	55(9)
C(18)	5197(14)	4100(10)	5327(7)	48(8)
C(19)	4295(13)	3983(9)	5217(7)	38(7)
C(20)	3848(10)	3361(8)	4760(6)	26(6)
C(21)	2439(11)	3779(9)	4994(7)	34(7)
C(22)	1496(13)	3524(9)	4746(7)	33(7)
C(23)	1121(12)	2875(9)	4269(6)	33(7)
C(24)	203(13)	2739(11)	4098(7)	46(8)
C(25)	−346(12)	3260(10)	4424(8)	46(8)
C(26)	55(11)	3885(10)	4914(8)	41(8)
C(27)	4122(10)	−77(8)	3631(6)	24(6)
C(28)	4518(10)	−585(8)	3995(6)	22(6)
C(29)	4070(10)	−647(8)	4485(6)	29(6)
C(30)	4414(12)	−1075(10)	4861(7)	42(8)
C(31)	5167(12)	−1444(9)	4730(7)	38(7)
C(32)	5594(11)	−1406(9)	4224(7)	36(7)
C(33)	5259(10)	−985(8)	3859(6)	26(6)
C(34)	6436(10)	−1332(10)	3226(7)	37(7)
C(35)	6756(11)	−1182(9)	2658(6)	32(7)
C(36)	7449(13)	−1547(11)	2407(8)	59(9)
C(37)	7769(12)	−1355(11)	1907(8)	57(9)
C(38)	7356(11)	−826(10)	1672(7)	40(7)
C(39)	6632(10)	−503(9)	1915(6)	31(7)
C(40)	4164(10)	−564(8)	1582(6)	25(6)
C(41)	4592(10)	−1254(9)	1191(6)	29(6)
C(42)	4899(11)	−1211(10)	644(7)	44(7)
C(43)	5321(13)	−1860(11)	307(8)	63(9)
C(44)	5442(12)	−2496(11)	526(8)	55(9)
C(45)	5123(11)	−2552(9)	1063(8)	45(8)
C(46)	4698(10)	−1909(9)	1386(6)	31(6)
C(47)	4357(12)	−2570(9)	2127(7)	45(7)
C(48)	3769(12)	−2474(9)	2648(7)	37(7)
C(49)	3074(12)	−2018(9)	2716(7)	40(7)
C(50)	2596(12)	−1989(9)	3209(8)	45(8)
C(51)	2840(12)	−2374(10)	3628(8)	46(8)
C(52)	3555(13)	−2811(10)	3535(8)	52(8)
C(53)	1198(9)	1208(8)	2567(6)	24(6)
C(54)	349(12)	1621(9)	2532(6)	26(7)
C(55)	−487(13)	1232(11)	2549(6)	43(8)
C(56)	−1224(12)	1671(16)	2540(8)	63(10)
C(57)	−1153(20)	2411(17)	2539(9)	82(13)
C(58)	−300(16)	2832(11)	2530(7)	49(8)
C(59)	424(12)	2415(10)	2538(6)	40(7)
C(60)	1489(15)	3596(10)	2668(8)	61(10)
C(61)	2495(16)	3816(9)	2790(6)	46(8)
C(62)	3067(14)	3276(11)	2922(7)	48(8)
C(63)	3965(15)	3507(10)	3018(7)	47(9)
C(64)	4292(17)	4293(13)	2990(9)	72(11)
C(65)	3692(18)	4757(13)	2868(9)	82(11)
C(66)	3759(9)	1619(8)	1793(6)	21(6)
C(67)	3964(10)	2313(8)	1542(5)	19(6)

(to be continued)

Table 2 (*continued*)

Atom	x	y	z	B_{eq}
C(68)	4829(12)	2671(9)	1635(6)	30(7)
C(69)	5108(11)	3339(9)	1439(7)	34(7)
C(70)	4466(13)	3630(9)	1141(7)	36(7)
C(71)	3566(12)	3275(9)	1019(7)	34(7)
C(72)	3320(9)	2626(8)	1239(6)	22(6)
C(73)	1760(11)	2647(10)	900(7)	37(7)
C(74)	879(12)	2224(9)	942(6)	27(6)
C(75)	92(4)	2513(10)	869(7)	39(8)
C(76)	−706(15)	2106(12)	908(7)	50(9)
C(77)	−735(10)	1330(11)	987(6)	41(7)
C(78)	73(10)	1057(10)	1067(6)	37(7)
C(79)	2158(11)	1126(10)	4711(7)	49(8)
Cl(1)	8011(3)	4586(3)	5728(2)	48(2)
O(1A)	7785(10)	3888(9)	5892(7)	94(5)
O(2A)	7352(9)	5125(8)	5900(6)	71(4)
O(3A)	8856(8)	4996(7)	6012(5)	52(3)
O(4A)	8004(7)	4369(6)	5070(5)	50(3)
Cl(2)	−564(3)	−1230(2)	723(2)	39(2)
O(5A)	210(10)	−1086(8)	438(6)	78(4)
O(6A)	−743(9)	−2039(8)	680(6)	80(4)
O(7A)	−460(8)	−718(6)	1342(5)	53(3)
O(8A)	−1281(10)	−1066(9)	371(7)	96(5)
Cl(3)	2272(3)	2826(3)	6317(2)	50(2)
O(9A)	2427(9)	3137(7)	6983(6)	72(4)
O(10A)	1992(8)	1967(7)	6145(5)	51(3)
O(11A)	1602(9)	3206(8)	6070(6)	78(4)
O(12A)	3106(9)	2979(7)	6079(5)	60(3)
Cl(4)	7096(3)	4626(3)	8620(2)	58(2)
O(13A)	7707(9)	5274(8)	8551(6)	79(4)
O(14A)	6833(10)	4866(8)	9235(6)	85(4)
O(15A)	7499(8)	3892(7)	8510(5)	64(3)
O(16A)	6319(9)	4492(7)	8173(6)	71(4)
Cl(5)	6566(4)	1274(3)	1266(3)	78(3)
O(17A)	7177(9)	688(8)	1143(6)	72(4)
O(18A)	6862(10)	1930(9)	1103(6)	87(4)
O(19A)	5723(14)	912(10)	1127(8)	116(6)
O(20A)	6600(9)	1647(8)	2001(6)	82(4)
Cl(6)	7551(3)	1033(3)	3991(2)	61(2)
O(21A)	7458(10)	585(9)	4404(7)	100(5)
O(22A)	8336(11)	1600(9)	4193(7)	98(5)
O(23A)	7657(9)	491(8)	3404(6)	77(4)
O(24A)	6772(9)	1458(8)	3931(6)	72(4)
Cl(7)	9357(6)	4664(4)	1399(3)	115(4)
O(25A)	8996(26)	3920(25)	898(19)	300(17)
O(26A)	9287(38)	4356(34)	1848(28)	416(29)
O(27A)	8894(17)	5181(16)	1158(12)	193(10)
O(28A)	10277(22)	4907(18)	1363(13)	217(12)
O(1W)	4601(8)	3687(7)	6984(5)	62(3)
O(2W)	9101(9)	5114(8)	9754(6)	83(4)
O(3W)	7358(13)	3567(11)	2002(9)	137(6)
O(4W)	5000	5000	0	193(13)
O(1S)	7311(16)	232(14)	9887(11)	178(9)
O(2S)	9513(8)	230(7)	5799(5)	62(3)
O(3S)	8552(9)	4814(8)	3876(6)	77(4)
O(4S)	8890(9)	1506(8)	5531(6)	80(4)
O(5S)	8380(14)	4452(12)	7424(9)	145(7)
O(6S)	6954(16)	3974(15)	3225(10)	175(8)
O(7S)	4099(18)	4182(15)	8164(12)	196(10)
O(8S)	2508(26)	3616(22)	9405(17)	294(16)
C(1S)	6496(22)	−474(20)	9847(15)	153(12)
C(2S)	10522(15)	135(12)	5827(9)	77(6)
C(3S)	9015(15)	5005(13)	3371(10)	86(7)
C(4S)	9504(15)	2248(13)	5603(10)	87(7)
C(5S)	8981(19)	3957(16)	7192(12)	113(9)
C(6S)	6770(22)	3236(21)	3350(15)	154(12)
C(7S)	3294(28)	4529(23)	8302(18)	189(15)
C(8S)	1528(27)	3530(23)	9790(18)	191(15)

Results and Discussion

A new ligand, 2-(pyrid-2-ylmethoxy)benzoic acid, contains the nitrogen base and the carboxy group linked through the molecular fragment, which was chosen so that the carboxylate ligand retained its ability to bind two iron ions together into the binuclear μ-oxo complex (see Fig. 1) upon chelation of this ligand to Fe^{III}. Complexation of 2-(pyrid-2-ylmethoxy)benzoic acid with iron ions was studied in a methanolic solution under conditions suitable for self-association of binuclear complexes.[11] However, regardless of conditions (the change in the ratio of the reagents, the temperature, the alkalinity of the medium, and the addition of water), brown crystals of trinuclear carboxylate complex **1** always formed. Complex **1** is very similar to benzoate and substituted benzoate trinuclear clusters of Fe^{III} obtained previously in the spectral and magnetic characteristics. The IR spectrum of the 0.01 *M* solution of **1** in acetonitrile shows the band of the C=O vibration of free acid (1760 cm^{-1}), which indicates that the ligand can dissociate in a solution. The shift of the absorption maximum of pyridine to the long-wavelength region by 8 cm^{-1} is indicative of the protonation of pyridine rings due to which the solubility of the complex in less polar solution decreases.

The IR spectra of the carboxylate complexes are characterized by two strong absorption bands of the C=O stretching vibrations between 1350 and 1650 cm^{-1}: ν_s = 1400—1450 cm^{-1} and ν_{as} = 1550—1650 cm^{-1}. The difference $\Delta\nu = \nu_{as} - \nu_s$ characterizes the mode of coordination of the carboxylate ligand. In the case of **1**, $\Delta\nu$ = 200 cm^{-1}, which falls outside the limits of the values usually observed for the bridging carboxylate group ($\Delta\nu$ = 160—140 cm^{-1}). An increased value of $\Delta\nu$ for **1** is attributable to inequivalence of the C—O bonds of the carboxylate bridge with different iron atoms (see below). The absorption at 560 cm^{-1} is absent in the initial compounds; according to the published data, this absorption can be assigned to ν_{as} Fe_3O.

The study of the complex by Mössbauer spectroscopy demonstrated that iron(III) atoms occur in this complex in the high-spin state (δ = 0.52 mm s^{-1} at 77 K). A relatively small value of the magnetic moment (μ_{eff}/at. Fe = 4.30 μ_B at 288 K) compared to that expected for high-spin Fe^{III} (5.9 μ_B) and a decrease in this value with decreasing

Table 3. Principal geometric parameters of the $[(MeOH)(H_2O)_2Fe_3(\mu_3\text{-}O)(\mu\text{-}OOCC_6H_4OCH_2C_6H_4NH)_6]^{7+}$ cation

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Fe(1)—O	1.883(8)	O(7)—C(27)	1.259(17)	O—Fe(1)—O(2)	96.5(4)	O(11)—Fe(2)—O(17)	92.4(4)
Fe(1)—O(2)	1.995(9)	O(8)—C(27)	1.277(18)	O—Fe(1)—O(10)	97.7(4)	O—Fe(2)—O(20)	177.2(4)
Fe(1)—O(10)	2.040(9)	O(10)—C(40)	1.257(17)	O(2)—Fe(1)—O(10)	89.5(4)	O(5)—Fe(2)—O(20)	85.5(4)
Fe(1)—O(14)	2.009(10)	O(11)—C(40)	1.234(14)	O—Fe(1)—O(14)	95.9(3)	O(8)—Fe(2)—O(20)	83.4(4)
Fe(1)—O(16)	2.017(10)	O(13)—C(53)	1.244(16)	O(2)—Fe(1)—O(14)	88.4(4)	O(11)—Fe(2)—O(20)	81.2(3)
Fe(1)—O(21)	2.093(8)	O(14)—C(53)	1.262(16)	O(10)—Fe(1)—O(14)	166.3(3)	O(17)—Fe(2)—O(20)	85.8(4)
Fe(2)—O	1.905(9)	O(16)—C(66)	1.266(15)	O—Fe(1)—O(16)	94.7(4)	O—Fe(3)—O(1)	93.3(3)
Fe(2)—O(5)	1.974(8)	O(17)—C(66)	1.269(17)	O(2)—Fe(1)—O(16)	168.6(4)	O—Fe(3)—O(4)	97.0(3)
Fe(2)—O(8)	2.002(11)	O(19)—C(79)	1.436(16)	O(10)—Fe(1)—O(16)	91.3(4)	O(1)—Fe(3)—O(4)	168.6(4)
Fe(2)—O(11)	2.039(8)	N(1)—C(9)	1.326(19)	O(14)—Fe(1)—O(16)	88.2(4)	O—Fe(3)—O(7)	93.4(4)
Fe(2)—O(17)	1.990(11)	N(1)—C(13)	1.348(26)	O—Fe(1)—O(21)	175.8(4)	O(1)—Fe(3)—O(7)	92.7(4)
Fe(2)—O(20)	2.098(9)	N(2)—C(22)	1.376(21)	O(2)—Fe(1)—O(21)	87.0(4)	O(4)—Fe(3)—O(7)	91.7(4)
Fe(3)—O	1.914(9)	N(2)—C(26)	1.325(20)	O(10)—Fe(1)—O(21)	84.7(3)	O—Fe(3)—O(13)	93.4(4)
Fe(3)—O(1)	1.997(8)	N(3)—C(35)	1.328(21)	O(14)—Fe(1)—O(21)	81.7(3)	O(1)—Fe(3)—O(13)	88.9(4)
Fe(3)—O(4)	2.017(7)	N(3)—C(39)	1.352(20)	O(16)—Fe(1)—O(21)	81.8(4)	O(4)—Fe(3)—O(13)	85.6(4)
Fe(3)—O(7)	1.982(10)	N(4)—C(48)	1.323(23)	O—Fe(2)—O(5)	97.1(4)	O(7)—Fe(3)—O(13)	173.0(4)
Fe(3)—O(13)	2.005(10)	N(4)—C(52)	1.327(23)	O—Fe(2)—O(8)	95.5(4)	O—Fe(3)—O(19)	178.6(3)
Fe(3)—O(19)	2.043(9)	N(5)—C(61)	1.304(21)	O(5)—Fe(2)—O(8)	91.2(4)	O(1)—Fe(3)—O(19)	85.3(3)
O(1)—C(1)	1.290(15)	N(5)—C(65)	1.311(30)	O—Fe(2)—O(11)	96.2(3)	O(4)—Fe(3)—O(19)	84.4(3)
O(2)—C(1)	1.246(19)	N(6)—C(74)	1.364(20)	O(5)—Fe(2)—O(11)	166.6(4)	O(7)—Fe(3)—O(19)	86.6(4)
O(4)—C(14)	1.260(16)	N(6)—C(78)	1.338(19)	O(8)—Fe(2)—O(11)	86.0(4)	O(13)—Fe(3)—O(19)	86.7(4)
O(5)—C(14)	1.263(16)			O—Fe(2)—O(17)	95.2(4)	Fe(1)—O—Fe(2)	119.5(5)
				O(5)—Fe(2)—O(17)	87.9(4)	Fe(1)—O—Fe(3)	121.4(5)
				O(8)—Fe(2)—O(17)	169.2(4)	Fe(2)—O—Fe(3)	119.1(4)

temperature (μ_{eff}/at. Fe = 2.43 μ_B at 87 K) are indicative of the antiferromagnetic interaction between iron atoms in the complex; the values determined are close to those typical of analogous trinuclear complexes. Similarly, the value of the quadrupole splitting (ΔE_q = 0.45 mm s^{-1} at 77 K) agrees with the values known for analogous iron complexes (0.45—0.75 mm s^{-1}).

Unlike binuclear complexes, the redox behavior of trinuclear carboxylate complexes is poorly studied.[12] It was demonstrated[13] that in aqueous solutions, $Fe^{III} \rightarrow Fe^{II}$ reduction in the complexes of composition $[Fe^{III}{}_{3-n}Cr^{III}(OAc)_6(\mu_3\text{-}OH)_2]^+$ (n = 0—2) occurs in one three-electron stage with the decomposition of their structures and, apparently, with the formation of mononuclear acetate complexes of Fe^{II}. The products of reduction of trinuclear carboxylate complexes of iron are more stable in nonaqueous solutions. For example in MeCN, electroreduction of cationic $[Fe^{III}{}_3(O_2CR')_6(\mu_3\text{-}O)]^{m+}$ complexes (where m = 1 or 7 for the carboxylate ligand and the protonated aminocarboxylate ligand $R'CO_2$, respectively) occurs in two successive one-electron stages, the first of them being reversible.[14] This is indicative of the stability of the electrogenerated mixed-valence $Fe^{II}Fe^{III}{}_2$ complex at least within the cyclic voltammetry time scale. The possibility of three-electron reduction of trinuclear carboxylate complexes of iron was not documented.[14]

The cyclic voltammograms of complex **1** in MeCN at ambient temperature show three diffusion-controlled ($I_p \cdot \upsilon^{-1/2}$ = const, where I_p is the peak height, and υ is the rate of the linear potential scan) rather broad ($E_p - E_{p/2}$ = 140—160 mV, where E_p and $E_{p/2}$ are the potentials at the peak maximum and at the half-height, respectively), irreversible peaks with approximately equal heights (Fig. 2) with the potentials (E_p) −0.02, −0.75, and −1.45 V (a saturated calomel electrode), respectively. The height of each peak observed is comparable with that of the one-electron peak of the oxidation of dodecylferrocene, all other factors being the same, which provides evidence that the three-electron reduction of complex **1** occurs in stages. The choice of dodecylferrocene, instead of ferrocene, as a standard is dictated by more similar dimensions and, therefore, closer values of the diffusion coefficients for this compound and **1**.

The irreversible character of the peaks (the absence of the corresponding anode responses in the anodic branches of the cyclic voltammograms) is retained when the temperature decreases to −35 °C. In principle, this may be evidence that the reduced mixed-valence forms of the complex studied are unstable (the *EC* process with the formation of the products electrounreactive in the potential range studied) and/or that the stage of electron transfer is decelerated because of a substantial structural rearrangement of the complex, which accompanies this stage.[15] However, it should be noted that the stepwise reduction of **1** is unlikely to be accompanied by destruction of the trinuclear structure of the complex, at least within the voltammetry time scale. If this were not so, probable products of decomposition of complex **1** reduced in a one-electron process, namely, mono- and/or binuclear Fe^{II} complexes, would be reduced at substantially more positive potentials than those of the second and third peaks (see above).[12]

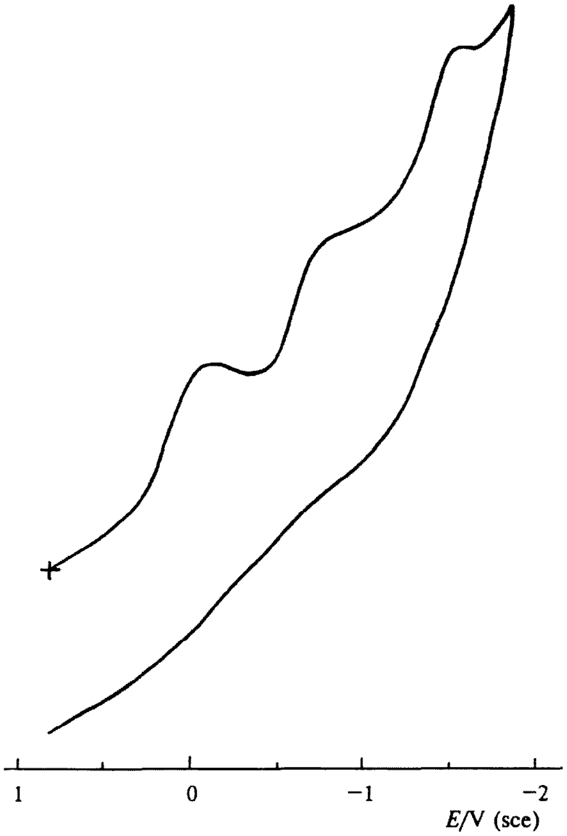

Fig. 2. Cyclic voltammograms of complex **1** ($1 \cdot 10^{-3}$ mol L^{-1}) in MeCN/0.1 *M* Bu_4NPF_6 on a Pt electrode (υ = 0.2 V s^{-1}) at 15 °C.

The stepwise rather than one-step reduction is indicative of the electronic interaction between iron atoms in the ground and mixed-valence states of complex **1**. This interaction may occur either "through a bond" with the participation of the μ_3-O atom or "through space" *via* the direct exchange between metal atoms, because, according to the X-ray structural data (see below), the Fe...Fe distance in the complex (3.3 Å) is only slightly larger than the sum of the covalent radii of the iron atoms (2.7 Å, see Ref. 16). When this interaction occurs, the electron density of Fe^{II} in the mixed-valence complexes delocalizes also on other Fe^{III} atoms resulting in the reduction of the latter at more negative potentials. To a first approximation, the degree of electronic interaction in the mixed-valence forms of the complex can be estimated from the value of the difference between the peak potentials (ΔE_p) observed.[17] For the $Fe^{II}Fe^{III}{}_2$ and $Fe^{II}{}_2Fe^{III}$ mixed-valence states, the values of the degree of electronic interaction (equal to ΔE_p) are −0.73 and −0.70 eV, respectively, which is indicative of a rather high degree of electronic exchange between iron atoms. For comparison, the degree of electronic interaction for the $Fe^{II}Fe^{III}{}_2$ state in most of the isostructural trinuclear carboxylate iron complexes studied[14] are −(0.6—0.8) eV depending on the nature of the carboxylate ligand, which is close to the value determined in this work.

According to the data of X-ray structural analysis, antiferromagnetic crystals of **1** (μ'_{eff}/at. Fe = 4.30 (288 K)—2.43 (87 K) μ_B) contain the trinuclear hepta-

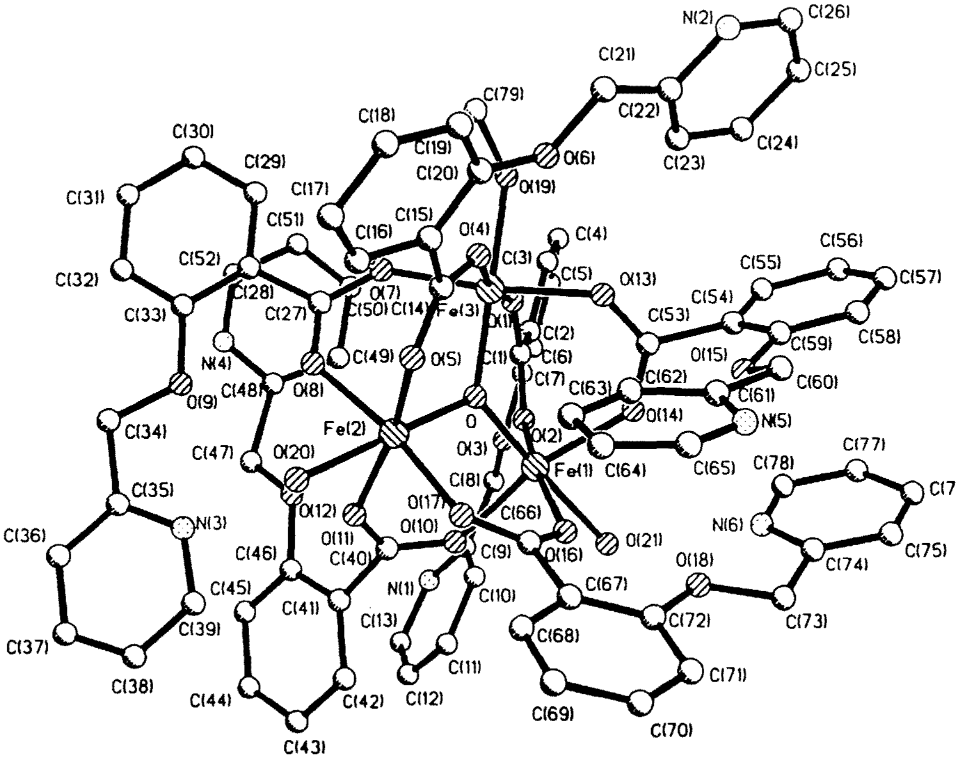

Fig. 3. Structure of the Fe_3O cluster of **1** determined by X-ray structural analysis.

charged cation $[(MeOH)(H_2O)_2Fe_3(\mu_3\text{-}O)(\mu\text{-}OOCC_6H_4OCH_2C_5H_4NH)_6]^{7+}$ (Fig. 3), seven perchlorate anions, eight methanol solvate molecules, and 3.5 water solvate molecules (three of them are in general positions, and one molecule occupies the crystallographic inversion center, see Table 2). The cation contains a virtually planar Fe_3O metal fragment (Fe—O 1.883(8), 1.905(9), and 1.914(9) Å) without metal—metal bonds (Fe...Fe 3.272(4), 3.312(4), and 3.291(4) Å); each pair of iron(III) atoms in this fragment is additionally bonded through two carboxylate bridges (Fe—O(OOCR) 1.974(8)—2.039(8) Å). Two metal atoms are coordinated to terminal water molecules (Fe—O(H_2O) 2.098(9) and 2.093(8) Å); the third metal atom is coordinated to an alcohol molecule (Fe—O(MeOH) 2.043(9) Å). As a result, the principal geometric characteristics of the cation of **1** (see Fig. 3, Table 3) are close to the values observed in the trinuclear Fe^{III} oxo-clusters, $L_3Fe_3O(OOCR)_6^+$ (L, R: H_2O, Me;[18,19] MeOH, Ph;[20] or MeOH, CMe_3;[21] $L_3 = (H_2O)(MeOH)_2$, R = Ph [22]), studied previously. However, note that the presence of pyridine rings in carboxylate ligands of **1** results in protonation of these rings in the course of the reaction, which essentially increases the total charge of the cluster cation (to +7). Analogous compounds were prepared previously with the use of amino acids.[23—25] In **1**, four of six NH^+ groups formed interact (through hydrogen bonds) with two alcohol solvate molecules and two water solvate molecules ($^+$NH...HOH 1.95 and 1.79 Å; $^+$NH...HOMe 1.76 and 1.87 Å). In addition, terminal ligands bonded to iron atoms in the cation are also involved in hydrogen bonding. Water molecules interact with anions (O(20)—H(20A)...O(24A) 2.22 Å, O(20)—H(20B)...O(20A) 2.40 Å, and O(21)—H(21A)...O(5A) 2.48 Å) and one alcohol solvate molecule (O(21)—H(21D)...O(4S) 1.77 Å); the coordinated MeOH molecule forms hydrogen bonds with a methanol solvate molecule (O(19)—H(19B)...O(2S) 1.83 Å). Taking into account that the remaining solvate molecules and perchlorate anions are also involved in weak hydrogen bonds, a complex network of particles participating in nonbonded interactions occurs in the crystal. Apparently, this leads to a weak field dependence of χ_m observed, although the presence of microimpurities of ferromagnetic iron compounds, which are formed at the crystal surface (particularly, small crystals) in the course of growth, can not be ruled out. However, when these insignificant factors were ignored, calculations of the exchange parameter $-2J$ within the framework of the Heisenberg—Dirac—Van Vlek model for symmetrical $Fe^{III}{}_3$ triangle ($S_1 = S_2 = S_3 = 5/2$) gave the value of 28 cm^{-1}, which is close to those known for this class of compounds.

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