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Chemical design of heterometallic carboxylate structures with Fe^{3+} and Ag^{+} ions as a rational synthetic approach

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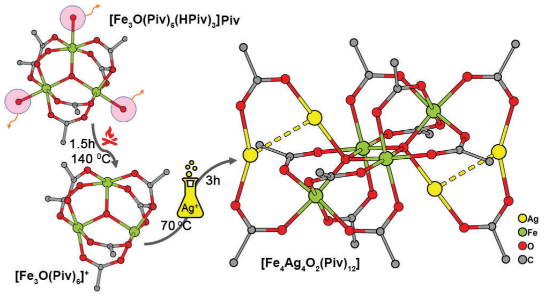
Solid phase thermolysis of pivalate complex $[Fe_3O(Piv)_6(HPiv)_3]Piv$ generates the $[Fe_3O(Piv)_6]^+$ complex cation due to a deficiency of ligands in the coordination sphere of the metal ions. Crystallization of $[Fe_3O(Piv)_6]^+$ from THF–EtOH leads to the heteroleptic complex $[Fe_3O(Piv)_6(THF)(EtOH)(OH)]\cdot 0.5\,THF\cdot 0.5\,H_2O$ in 69% yield, while the reaction of $[Fe_3O(Piv)_6]^+$ with $AgNO_3$ in toluene results in the complex $[Fe_4Ag_4O_2(Piv)_{12}]\cdot 2\,PhMe$ with a rare combination of Fe^{III} and Ag^{I} atoms. Crystal structures of the two new complexes have been established.



Keywords: iron complex, solid phase thermolysis, heteroleptic complex, silver, crystal structure.

Iron complexes occupy a prominent place among polynuclear coordination compounds,[1,2] because they participate in biochemical processes as parts of enzymes and hemoglobin, serve as catalysts in the conversion of natural gas as well as are employed in production of advanced materials like thermostable layered systems or superconductors.[3,4] Polynuclear complexes in general exhibit remarkable catalytic, sorption, magnetic, optical and/or conductive properties as well as represent promising components for new-generation functional molecular materials and convenient precursors for the targeted thermal synthesis of inorganic substances, including the nanoscale ones.[5–12] Therefore, it is desirable to expand the range of similar objects, namely various types of polynuclear architectures with ions of iron and other metals, for their further targeted selection. Typically, trinuclear structures like $[Fe_3O(OOCR)_6L_3]^+X^-$ are employed for a design of iron polynuclear clusters.[13–16] However, in the synthesis of heteronuclear oxo-carboxylate Fe^{III} compounds, a stable trinuclear moiety $\{Fe_2M–\mu^3\text{-}O\}$ is formed as a basic motif, which complicates subsequent chemical modifications, in particular formation of heteronuclear fragments of greater nuclearity. We suggested a method for the synthesis of heteronuclear pivalate (Piv) complexes $[Fe^{III}_2M^{II}_xO(Piv)_6(L)_3]$, where M^{II} = Mn, Ni or Zn, x = 1 or 4 and L = H_2O, Et_2O, HPiv or 1,10-phenanthroline,[17–19] based on an ion-exchange reaction of M^{II} salts, an alkali and HPiv followed by solid phase thermolysis of the resulting intermediate in Ar or air. However, this method has been found unsuitable for the synthesis of complexes with an $\{Fe^{III}Li^{I}\}$ moiety, where a ‘functional block’ technique is used.[20,21] In this work, we developed a method for a synthesis of the functional blocks with Fe^{III} atoms, including the $\{Fe^{III}Ag^{I}\}$ heterometallic moiety. Analysis of CCDC structural data by November, 2020 revealed the presence of only two oxo-compounds with Fe and Ag atoms.[22,23] Therefore, the search for synthetic approaches for this combination of atoms represents a relevant goal.

Initial complex **1** of composition $[Fe_3O(Piv)_6(HPiv)_3]Piv$ was synthesized similarly to the known ones[24] and subjected to solid phase thermolysis at 140 °C for 90 min in the air to remove neutral HPiv molecules (taking into account the boiling point of HPiv equal to 164 °C) and create a coordination deficit at the metal centers. The conversion of complex **1** into product **2**[†] was followed using IR spectra (Figure 1).

The bands at 1702, 1303, 869 and 768 cm^{-1} were chosen as indicators of the removal of coordinated HPiv molecules since they corresponded to C=O and C–O vibrations as well as bending vibrations of the OH groups of HPiv. The transformation was confirmed as well gravimetrically, the mass of desorbed HPiv was 0.68 g (34.0%), which matched the calculated value of 34.7% with respect to original complex **1**. Subsequent crystallization of amorphous thermolyzed product **2** from a

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[†] HPiv (30 g, 0.29 mol) and KOH (6 g, 0.11 mol) were dissolved in water (40 ml) at 50 °C, then an aqueous solution of $Fe(NO_3)_3\cdot 9\,H_2O$ (10 g, 0.025 mol) was added. The mixture was stirred for *ca.* 15 min. The oily layer formed was separated by decantation and extracted with diethyl ether. Evaporation of the solvent gave a solid mass, which was washed with MeCN for removal of residual HPiv, resulting in complex **1**. IR (ATR, ν/cm^{-1}): 2964 (m), 2931 (w), 2872 (w), 1696 (s), 1578 (vs), 1561 (vs), 1482 (vs), 1459 (w), 1423 (vs), 1405 (vs), 1379 (m), 1357 (vs), 1331(w), 1227 (vs), 1201 (vs), 1032 (w), 939 (m), 899 (m), 870 (m), 787 (s), 768 (w), 653 (w), 602 (w), 590 (vs), 539 (m), 438 (vs), 425 (vs).

Complex **1** was kept in a porcelain beaker in air at 140 °C for 90 min with shaking of the content at 30 min intervals affording complex **2**. IR (ATR, ν/cm^{-1}): 2962 (m), 2929 (w), 2872 (w), 1557 (vs), 1482 (vs), 1457 (w), 1420 (vs), 1379 (vs), 1360 (vs), 1032 (w), 939 (w), 787 (m), 595 (vs), 512 (m), 443 (vs), 426 (vs).

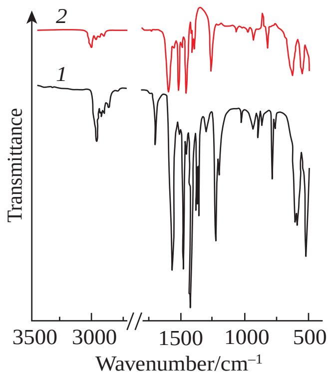


Figure 1 IR spectra of (*1*) complex **1** as an amorphous phase before thermolysis and (*2*) complex **2** as a product of the thermolysis.

THF–EtOH mixture gave tricyclic complex **3** of composition $[Fe_3O(Piv)_6(THF)(EtOH)(OH)]\cdot 0.5THF\cdot 0.5H_2O$ (Figure 2),[‡] while interaction of compound **2** with silver nitrate in toluene gave coordination compound **4** of composition $[Fe_4Ag_4O_2(Piv)_{12}]$ (Scheme 1).[§]

According to X-ray data,[¶] complex **3** crystallizes as a solvate with half THF and half water molecules. The structure of complex **3** is a nontrivial one because three different co-ligands, namely THF, EtOH and HO⁻, are coordinated to three Fe^{III} atoms in a μ^3-O metal oxide core (see Figure 2), this type of heteroleptic coordination to Fe^{3+} is observed for the first time. Each Fe atom is located in an octahedral environment composed of O_2^- residues of Piv⁻, THF, EtOH and the OH⁻ group.

Complex **4** crystallizes as a solvate with two toluene molecules, the complex molecule being centrosymmetric. The center of inversion is located between the Fe(1), O(1M), Fe(1A) and O(1MA) atoms, where the ‘A’ index corresponds to the symmetry element $-x + 1, -y + 1, -z + 1$ (Figure 3). Note, that in all the known analogous structures an alkali metal atom is bound to oxygen atoms of the μ_3-oxo group and the bridging carboxylate groups.

The metal–ligand core formation in complex **4** is similar to the reported Fe–Li and Fe–Na carboxylate compounds.[27]

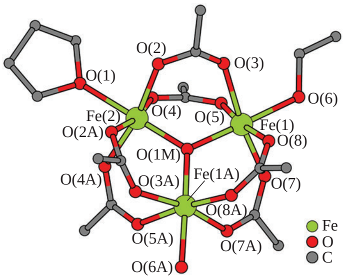
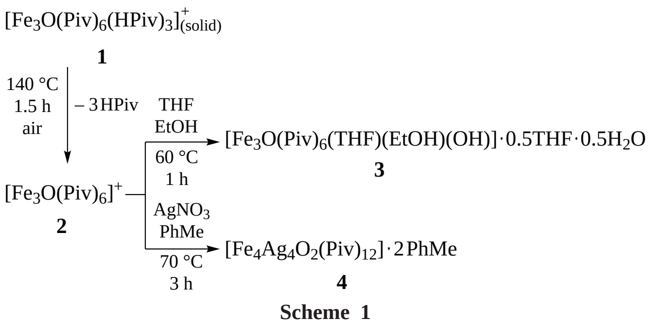


Figure 2 Molecular structure of complex **3**, H atoms and the Me groups of Bu^t moieties are omitted for clarity. Selected bond lengths and interatomic distances (Å): Fe–O(μ^3O) 1.864(8)–1.924(4), Fe–O(Piv) 1.958(3)–2.096(3), Fe–O(THF) 2.1115(1), Fe–O(OH/EtOH) 2.048(7), Fe···Fe 3.286(2)–3.324(4).



Scheme 1

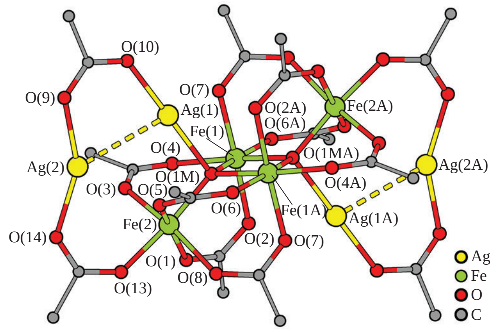


Figure 3 Molecular structure of the metal–carboxylate core in complex **4**, H atoms and the Me groups of Bu^t moieties are omitted for clarity. Selected bond lengths and interatomic distances (Å): Fe–O(μ^3O) 1.925(4)–1.960(2), Ag–O(μ^3O) 2.216(3), Fe–O(Piv) 1.965(4)–2.153(3), Ag–O(Piv) 2.079(3)–2.155(2), Fe···Fe 3.0032(7)–3.367(4), Fe···Ag 3.201(5)–3.380(2), Ag···Ag 3.088(2).

[‡] Solid sample of complex **2** (100 mg, 0.11 mmol) was dissolved in THF–EtOH (1 : 1, 40 ml) at 60 °C for 1 h. The resulting solution was slowly cooled to room temperature and kept for 24 h. The crystals precipitated were separated from the mother liquor by decantation and dried in air resulting in complex **3**. Yield 76 mg (69%). Found (%): C, 47.32; H, 7.76. Calc. for $C_{38}H_{74}Fe_3O_{17}$ (%): C, 47.03; H, 7.69. IR (ATR, ν/cm⁻¹): 2960 (m), 2931 (w), 2872 (w), 1696 (w), 1640 (w), 1612 (s), 1585 (br. s), 1567 (vs), 1545 (vs), 1482 (vs), 1417 (vs), 1357 (vs), 1222 (vs), 1031 (w), 938 (w), 895 (vs), 787 (m), 727 (m), 603 (vs), 551 (w), 435 (vs), 427 (vs), 419 (vs).

[§] Solid sample of complex **2** (100 mg, 0.11 mmol) and $AgNO_3$ (56 mg, 0.33 mmol) were dissolved in toluene at 70 °C and heated at this temperature for 3 h. The solution was slowly cooled to room temperature and kept for 48 h. The crystals precipitated were separated from the mother liquor by decantation and dried in air resulting in complex **4**. Yield 112 mg (45%). Found (%): C, 42.43; H, 5.67. Calc. for $C_{74}H_{124}Fe_4Ag_4O_{26}$ (%): C, 42.64; H, 5.99. IR (ATR, ν/cm⁻¹): 2969 (m), 2931 (w), 2873 (w), 1626 (m), 1569 (vw), 1534 (br. m), 1481 (s), 1422 (s), 1378 (w), 1360 (s), 1346 (s), 1219 (vs), 1085 (vw), 1031 (w), 938 (w), 872 (w), 789 (m), 733 (m), 696 (w), 643 (w), 598 (s), 554 (w), 514 (m), 459 (vs), 419 (br. m), 436 (br. m).

[¶] *Crystal data for* **3**. $C_{38}H_{74}Fe_3O_{17}$ (M = 970.52), orthorhombic, space group *Pnma*, at 120 K: a = 26.362(2), b = 11.7173(9) and c = 18.8062(14) Å, V = 5809.1(8) Å³, Z = 4. Total of 72543 reflections were collected, from which 3947 were independent. The final refinement parameters were R_1 = 0.1368 and wR_2 = 0.3817 for the reflections with $I > 2\sigma(I)$. GOOF 1.11. Maximum and minimum of residual electronic density were 0.124 and –1.013 eÅ⁻³.

Crystal data for **4**. $C_{74}H_{124}Fe_4Ag_4O_{26}$ (M = 2084.60), monoclinic, space group $P2_1/c$, at 296 K: a = 13.8804(6), b = 15.4889(8) and c = 22.0054(8) Å, V = 4571.7(3) Å³, Z = 2. Total of 40278 reflections were collected, from which 8169 were independent. The final refinement parameters were R_1 = 0.0325 and wR_2 = 0.0789 for the reflections with $I > 2\sigma(I)$. GOOF 1.022. Maximum and minimum of residual electronic density were 0.970 and –0.559 eÅ⁻³.

X-ray diffraction data were obtained on a Bruker APEX2 DUO CCD diffractometer with graphite monochromated MoKα radiation, λ = 0.71073 Å. The structures were solved by direct methods and refined in the full-matrix least-squares anisotropic approximation using the SHELX2014/4 and Olex2 software for complex **3** as well as the SHELXL-2018/3 one for complex **4**.[25,26] The H atoms of OH groups were located from the difference Fourier synthesis, positions of other H atoms were calculated. All the H atoms were then refined in isotropic approximation within the riding model. High values of R-factors for structure **3** resulted from poor reflective power of the best available crystal for this complex, the complex also suffered from a severe disorder of its organic ligands and solvent molecules.

CCDC 2033294 and 2033295 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Thus, the complexes $[Fe_4Li_2O_2(Piv)_{10}(H_2O)_2]$ and $[Fe_4Na_2O_2(Piv)_{10}LL']$, where L = MeCN, L′ = Me_2CO or L = L′ = HPiv, are formed on the platform of tetranuclear $[Fe_4O_2(O_2CR)_{10}]$ fragments based on bent arrangement of four ferric sites in the $\{Fe_4O_2\}$ units. Li or Na atoms are linked to the bridging oxo groups on one side of the plane of the $\{Fe_4O_2\}$ unit. In complex **4**, a similar situation is observed, but the alkali metal atom is substituted by the $\{Ag_2(\mu\text{-}Piv)\}$ moiety with Ag–O bond lengths of 2.079(3) and 2.155(2) Å, which is stabilized by an argentophilic interaction with Ag···Ag distance of 3.088(2) Å (see Figure 3). One of the possible ways of transformation of the basic fragment Fe_3 into the tetranuclear Fe_4 one consists in the dissociation of Fe–O bonds as a result of the initial heating in the presence of $AgNO_3$. Structure **4** exhibits symmetric bonding of the Ag atoms with oxo groups relative to the central Fe(1) and Fe(1A) atoms, *i.e.*, on the opposite sides of the Fe_4 plane. The combination of Ag and Fe ions bound through an O atom in the same molecule is a rare phenomenon, only two structures of this type having been found in the CCDC database as of November, 2020.[28] Namely, in the Fe^{III}–EDTA complex $[AgFe(EDTA)(H_2O)]\cdot 2H_2O$,[22] free O atoms of the coordinated carboxylate groups are bound to Ag atoms, thus forming a polymer structure. In another similar complex $\{Fe_2(\mu\text{-}OH)_2(ClO_4)_2(PIM)[2,6\text{-}(p\text{-tolyl})_2C_6H_3CO_2]Ag\}$, the $\{Fe_2(OH)_2\}$ unit and the Ag atom surrounded by donor atoms of a macrocyclic PIM ligand are linked through a μ_3-OH group.[23]

In summary, the employment of solid phase thermolysis combined with solution-based technique in the preparation of homo- and heteropolynuclear Fe^{III} complexes allows one to generate $\{Fe_3O/Fe_2MO\}$ metal oxide moieties,[18–21] which can enter chemical reactions with both metal salts and organic molecules resulting in new combinations of atoms, such as Fe^{III}–Ag^{I}.

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