ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2020, Vol. 46, No. 2, pp. 105–110. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Koordinatsionnaya Khimiya, 2020, Vol. 46, No. 2, pp. 98–103.

# Unusual Hexanuclear Fe(II, III) Pyrazole–Pyrazolate–Pivalate Formed upon $\eta^5$,$\pi$-Bonding of Bridging Pyrazolate Anion to Potassium Cation

**M. A. Uvarova**[a] **and S. E. Nefedov**[a], *
[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
**e-mail: snef@igic.ras.ru*

Received September 27, 2019; revised September 29, 2019; accepted September 30, 2019

**Abstract**—The reaction of aqueous iron(II) sulfate with potassium pivalate in MeCN followed by removal of the solvent and dissolution of the residue in $Et_3N$ and hexane gives a brown solution and a white precipitate. The reaction of the mother liquor with excess 3,5-dimethylpyrazole (HDmpz) afforded the hexanuclear complex $\{[Fe_3(\mu^3\text{-}O)(\mu\text{-}OOC^tBu)_4(OOC^tBu)_2(HDmpz)(\mu,\eta^5\text{-}Dmpz)(\mu\text{-}K)]_2 \cdot 2HDmpz\}$ (**I**). The complex was characterized by elemental analysis, IR spectroscopy, and X-ray diffraction (CIF file CCDC no. 1956015). Complex **I** is formed upon deprotonation of HDmpz, which was observed for the first time in the presence of iron carboxylates. Deprotonation gives the bridging pyrazolate anion, which assembles two trinuclear $Fe_3(\mu^3\text{-}O)(\mu\text{-}OOC^tBu)_4(OOC^tBu)_2(HDmpz)$ moieties into a hexanuclear cluster though unusual $\eta^5$,$\pi$-coordination with the potassium cation.

*Keywords:* iron(II, III) pivalates, bridging pyrazolate anion, $\eta^5$,$\pi$-coordination, potassium cation, synthesis, X-ray diffraction

**DOI:** 10.1134/S1070328420020074

## INTRODUCTION

Iron(II, III) complexes containing carboxylate anions and coordinated heterocyclic molecules (pyrazole or imidazole and their analogues) are often considered as structural analogues of the active parts of natural metalloenzymes responsible for various catalytic processes, first of all, reduction of H2O to H2, CO2 to CO, N2 to NH3, O2 to H2O, and so on [1–8].

In addition, such complexes are actively studied as potential molecular magnets, catalysts of various chemical reactions, and the rectants for the synthesis of unusual homo- and heterometallic materials, including finely dispersed materials of various grades formed upon reduction in a hydrogen atmosphere or thermolysis [9–11].

Previously, it was found that heterocyclic 3,5-dimethylpyrazole (HDmpz) can be deprotonated under mild conditions in the presence of simple lantern dimers $M_2(\mu\text{-}OOC^tBu)_4(NEt_3)_2$ (M = Zn, Co(II)) to give the bridging pyrazolate dimers $M_2(\mu\text{-}Dmpz)_2(HDmpz)_2(OOC^tBu)_2$, which are protonated with strong trifluoromethanesulfonic acid to give the complexes $[M_2(\mu\text{-}OOC^tBu)_2(HDmpz)_4]Otf_2$ containing the $MO_2N_2$ coordination unit, which is present in the active part of natural metalloenzymes [12].

This communication describes an approach to the synthesis of iron(II) pivalate-based pyrazolate-bridged complexes and structure of the product $\{[Fe_3(\mu^3\text{-}O)(\mu\text{-}OOC^tBu)_4(OOC^tBu)_2(HDmpz)(\mu,\eta^5\text{-}Dmpz)(\mu\text{-}K)]_2 \cdot 2HDmpz\}$ (**I**) formed in the reaction between aqueous iron sulfate and potassium pivalate in acetonitrile followed by the reaction with triethylamine and HDmpz.

## EXPERIMENTAL

All operations on the synthesis and isolation of the complex were carried out in a pure argon atmosphere using anhydrous solvents.

**Synthesis of complex I.** Dry powders of $FeSO_4 \cdot 7H_2O$ (1.00 g, 3.60 mM) and $KOOC^tBu$ (0.76 g, 5.42 mM) were placed into a two-necked flask, evacuated, and dissolved in anhydrous acetonitrile (20 mL). The obtained slightly brown-colored solution was filtered to remove a white precipitate. The filtrate was concentrated to dryness in water jet pump vacuum, and (partially soluble) $Et_3N$ (1 mL) and hexane (20 mL) were successively added. The brown solution was mixed with a solution of HDmpz (0.53 g, 5.51 mM) in hexane (5 mL). The reaction mixture was concentrated to ~15 mL and kept at room temperature for 24 h. The brown single crystals thus formed were

**Table 1.** Crystallographic parameters and structure refinement details for complex **I**

| Parameter | Value |
|---|---|
| *M* | 2433.77 |
| Color | Brown |
| *T*, K | 150(2) |
| System | Triclinic |
| Space group | $P\bar{1}$ |
| *a*, Å | 11.448(2) |
| *b*, Å | 14.618(3) |
| *c*, Å | 21.660(4)) |
| α, deg | 90.78(3) |
| β, deg | 97.58(3) |
| γ, deg | 110.31(3) |
| *V*, Å$^3$ | 3362.8(13) |
| *Z* | 1 |
| ρ(calcd.), mg/m$^3$ | 1.202 |
| μ, mm$^{-1}$ | 0.758 |
| *F*(000) | 1288 |
| Crystal size, mm | 0.24 × 0.22 × 0.20 |
| Range of θ, deg | 1.48–26.00 |
| Ranges of reflection indices | $-13 \le h \le 14$,<br>$-16 \le k \le 18$,<br>$-26 \le l \le 26$ |
| Number of reflections | 12781 |
| Number of unique reflections ($R_{int}$) | 3803 (0.1254) |
| GOOF | 0.908 |
| $R$ ($I > 2\sigma(I)$) | $R_1 = 0.0763$,<br>$wR_2 = 0.1738$ |
| *R* (for all reflections) | $R_1 = 0.2243$,<br>$wR_2 = 0.2305$ |
| Residual electron density (min/max), e/Å$^3$ | 0.570/–0.693 |

separated from the mother liquor by decantation, washed with cold hexane, and dried in an argon flow. The yield of the single crystalline product was 0.3 g (25%).

For $C_{100}H_{170}N_{12}O_{30}K_2Fe_6$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 49.35 | H, 7.04 | N, 6.91 |
| Found (powder), % | C, 48.02 | H, 6.95 | N, 4.88 |

IR (KBr; ν, cm$^{-1}$): 3021 w, 2957 w, 2870 w, 1591 m, 1567 m, 1524 w, 1483 m, 1419 s, 1355 m, 1333 m, 1304 m, 1224 s, 1082 s, 1032 s, 784 m, 735 m, 659 vw, 562 w.

IR spectra of crystalline samples were measured in the 4000–550 cm$^{-1}$ range in KBr pellets on a NEXUS FT IR spectrometer (NICOLET) with a MIRacle attachment (Pike Technologies) equipped with a diamond crystal.

**X-ray diffraction study of I** was carried out by a standard procedure on a Bruker SMART Apex II automated diffractometer equipped with a CCD array detector (Mo$K_\alpha$, λ = 0.71073 Å, graphite monochromator, ω scan mode) at $T$ = 150 K. The structure was solved using the SHELXTL PLUS software package (PC version) and refined using the SHELXTL-97 paclage [13–16]. The hexane molecule disordered over several positions was removed from the refinement using the SQUEEZE software. The crystal data and structure refinement details are summarized in Table 1 and key geometric parameters of the complex are in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1956015; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

The reaction of aqueous iron(II) sulfate with potassium pivalate (1 : 2) in acetonitrile at room temperature followed by complete removal of the solvent and dissolution of the residue in triethylamine and hexane afforded a brown solution and a white precipitate. The reaction of the thus obtained solution with excess HDmpz and crystallization at room temperature give hexanuclear complex **I** as brown single crystals in 25% yield.

According to X-ray diffraction data, in the independent part of cluster **I** (Fig. 1, Tables 1, 2), three iron atoms separated by nonbonding distances (Fe(1)···Fe(2), 3.2767(9); Fe(1)···Fe(3), 3.2501(9); Fe(2)···Fe(3), 3.2834(9) Å) are linked by the tridentate bridging oxygen atom (Fe(1)–O(15) 1.897(5), Fe(2)–O(15) 1.855(5), Fe(3)–O(15) 1.914(5)Å; the deviation of the O(15) atom from the $Fe_3$ plane is 0.030 Å). The Fe(2) atom containing an HDmpz molecule in the axial position (Fe(2)–N(1) 2.152(7) Å) is linked to each of the other two iron atoms by two μ-pivalate anions (Fe(2)–O 1.996(6)–2.012(6), Fe(1)–O 2.003(6), 2.036(6), Fe(3)–O 2.007(6), 2.024(6) Å) and has a distorted octahedral environment. The Fe(1) and Fe(3) atoms have analogous environment. Apart from the μ$^3$-oxygen atom and the oxygen atoms of the pivalate bridges (Fe(1)–O(5), 2.056(6); Fe(3)–O(6), 2.057(6) Å), it is formed by nitrogen atoms of the deprotonated bridging pyrazolate anion (Fe(1)–N(3), 2.105(7); Fe(3)–N(4), 2.084(7) Å) and by oxygen atoms of the terminal OOC$^t$Bu anion (Fe(1)–O(7), 1.935(6); Fe(3)–O(13), 1.949(5)Å). The uncoordinated oxygen atoms of the terminal pivalate anions

**Table 2.** Selected bond lengths and bond angles for complex **I**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Fe(1)–O(15) | 1.897(5) | Fe(1)–O(7) | 1.935(6) |
| Fe(1)–O(3) | 2.003(6) | Fe(1)–O(1) | 2.036(6) |
| Fe(1)–O(5) | 2.056(6) | Fe(1)–N(3) | 2.105(7) |
| Fe(2)–O(15) | 1.855(5) | Fe(2)–O(11) | 1.996(6 |
| Fe(2)–O(9) | 1.995(5) | Fe(2)–O(4) | 2.004(6) |
| Fe(2)–O(2) | 2.012(6) | Fe(2)–N(1) | 2.152(7) |
| Fe(3)–O(15) | 1.914(5) | Fe(3)–O(13) | 1.949(5) |
| Fe(3)–O(12) | 2.007(6) | Fe(3)–O(10) | 2.024(6) |
| Fe(3)–O(6) | 2.057(6) | Fe(3)–N(4) | 2.084(7) |
| Fe(3)–K(1) | 3.836(3) | K(1)–O(8) | 2.593(6) |
| K(1)–O(14) | 2.627(6) | K(1)–O(14) | 2.733(6) |
| K(1)–O(6) | 2.812(6) | K(1)–N(4) | 2.854(7) |
| K(1)–N(3) | 2.866(7) | K(1)–C(36) | 3.126(10) |
| K(1)–C(39) | 3.155(9) | K(1)–C(38) | 3.288(9) |
| K(1)–C(11) | 3.291(9) | K(1)–C(13) | 3.467(10) |
| K(1)–C(35) | 3.537(11) | O(14)–K(1)) | 2.627(6) |
| N(1)–N(2) | 1.325(8) | N(3)–N(4) | 1.373(8) |
| N(5)–N(6) | 1.322(10) | | |
| Angle | ω, deg | Angle | ω, deg |
| O(15)Fe(1)O(7) | 170.5(2) | O(15)Fe(1)O(3) | 96.9(2) |
| O(7)Fe(1)O(3) | 91.8(2) | O(15)Fe(1)O(1) | 94.4(2) |
| O(7)Fe(1)O(1) | 90.0(2) | O(3))Fe(1)O(1) | 86.1(2) |
| O(15)Fe(1)O(5) | 87.7(2) | O(7)Fe(1)O(5) | 84.6(2) |
| O(3)Fe(1)O(5) | 167.6(2) | O(1)Fe(1)O(5) | 82.0(2) |
| O(15)Fe(1)N(3) | 85.1(2) | O(7)Fe(1)N(3) | 92.0(3) |
| O(3)Fe(1)N(3) | 84.1(3) | O(1)Fe(1)N(3) | 170.1(3) |
| O(5)Fe(1)N(3) | 107.9(3) | O(15)Fe(2)O(11) | 96.5(2) |
| O(15)Fe(2)O(9) | 96.5(2) | O(11)Fe(2)O(9) | 88.4(2) |
| O(15)Fe(2)O(4) | 91.4(2) | O(11)Fe(2)O(4) | 89.3(2) |
| O(9)Fe(2)O(4) | 171.9(2) | O(15)Fe(2)O(2) | 93.5(2) |
| O(11)Fe(2)O(2) | 169.5(2) | O(9)Fe(2)O(2) | 87.3(2) |
| O(4)Fe(2)O(2) | 93.6(2) | O(15)Fe(2)N(1) | 171.0(2) |
| O(11)Fe(2)N(1) | 86.7(3) | O(9)Fe(2)N(1) | 92.0(3) |
| O(4-Fe(2)N(1) | 80.2(3) | O(2)Fe(2)N(1) | 83.9(3) |
| O(15-Fe(3)O(13) | 178.5(3) | O(15)Fe(3)O(12) | 95.0(2) |
| O(13-Fe(3)O(12) | 86.3(2) | O(15)Fe(3)O(10) | 92.1(2) |
| O(13)Fe(3)O(10) | 88.6(2) | O(12)Fe(3)O(10) | 88.9(2) |
| O(15)Fe(3)O(6) | 92.5(2) | O(13)Fe(3)O(6) | 86.2(2) |
| O(12)Fe(3)O(6) | 172.0(2) | O(10)Fe(3)O(6) | 88.3(2) |
| O(15)Fe(3)N(4) | 85.0(2) | O(13)Fe(3)N(4) | 94.2(2) |
| O(12)Fe(3)N(4) | 93.4(3) | O(10)Fe(3)N(4) | 176.4(3) |
| O(6)Fe(3)N(4) | 89.8(2) | O(15)Fe(3)K(1) | 101.06(16) |
| O(13)Fe(3)K(1) | 77.51(18) | O(12)Fe(3)K(1) | 134.63(17) |
| O(10)Fe(3)K(1) | 131.94(18) | O(6)Fe(3)K(1) | 45.61(16) |
| N(4)Fe(3)K(1) | 46.97(19) | O(8)K(1)O(14) | 110.2(2) |
| O(8K(1)O(14) | 151.1(2) | O(14)K(1)O(14) | 92.81(19) |
| O(8K(1)O(6) | 84.49(19) | O(14)K(1)O(6) | 155.03(18) |
| O(14)K(1)O(6) | 68.16(18) | O(8)K(1)N(4) | 98.01(19) |
| O(14)K(1)N(4) | 131.7(2) | O(14)K(1)N(4) | 77.84(19) |
| O(6)K(1)N(4) | 62.07(19) | O(8)K(1)N(3) | 71.90(19) |
| O(14)K(1)N(3) | 133.4(2) | O(14)K(1)N(3) | 105.3(2) |
| O(6)K(1)N(3) | 69.6(2) | N(4)K(1)N(3) | 27.77(17) |

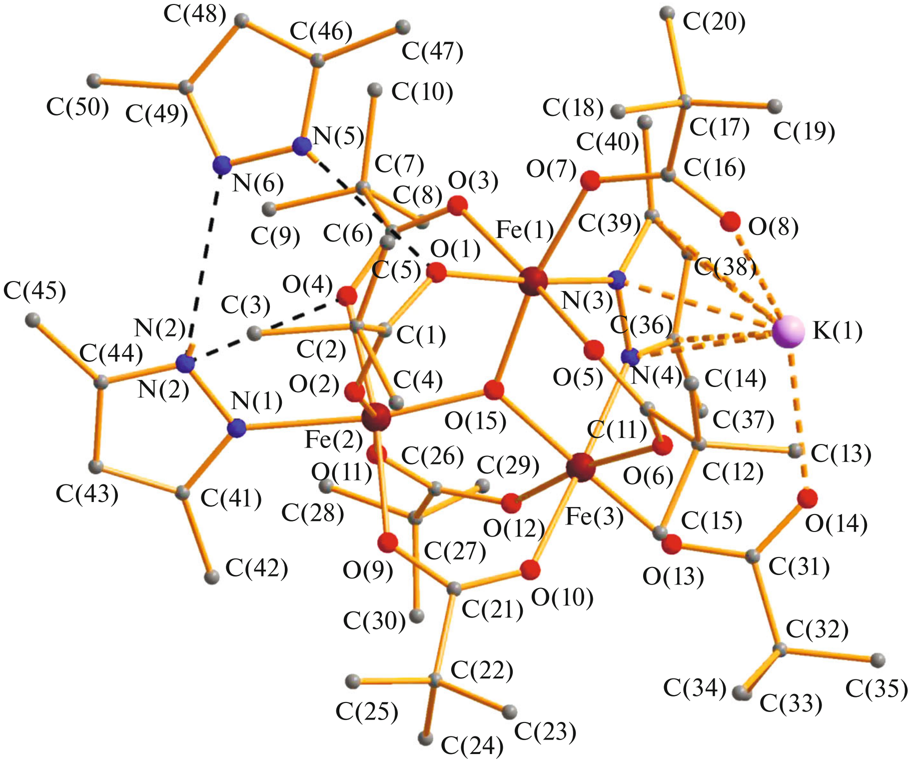

**Fig. 1.** Structure of the independent part of complex **I**.

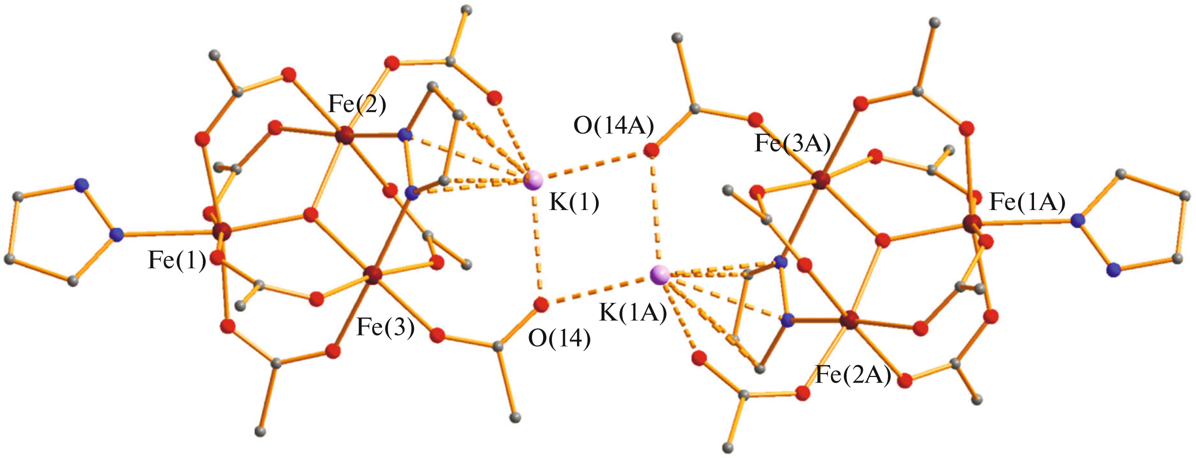

**Fig. 2.** Structure of cluster **I**. For clarity, only the central carbon atoms are shown for the *tert*-butyl substituents of carboxylate anions, and the methyl groups of HDmpz and hydrogen atoms are omitted. The oxygen atoms are shown in red, the nitrogen atoms are blue, and the carbon atoms are gray.

have contacts with the potassium cation (K(1)···O(8), 2.593(6); K(1)–O(14), 2.733(6) Å), which is coordinated in the $\eta^5,\pi$ fashion to delocalized $\pi$-electron density of bridging Dmpz (K(1)···N, 2.854(7), 2.866(7); K(1)···C, 3.126(10)–3.288(9) Å). The nitrogen–nitrogen bond in the pyrazolate anion (1.373(8) Å) is noticeably elongated compared with the bonds in coordinated (1.325(8) Å) and solvation pyrazoles (1.322(10) Å). The potassium cation is also bonded to the O(14*A*) oxygen atom (K(1)–O(14*A*), 2.627(6) Å), which belongs to another molecule of the $Fe_3$ triangle, thus furnishing hexanuclear cluster **I** (Fig. 2).

The unit cell of complex **I** contains two pyrazole solvate molecules, the NH groups of which are hydro-

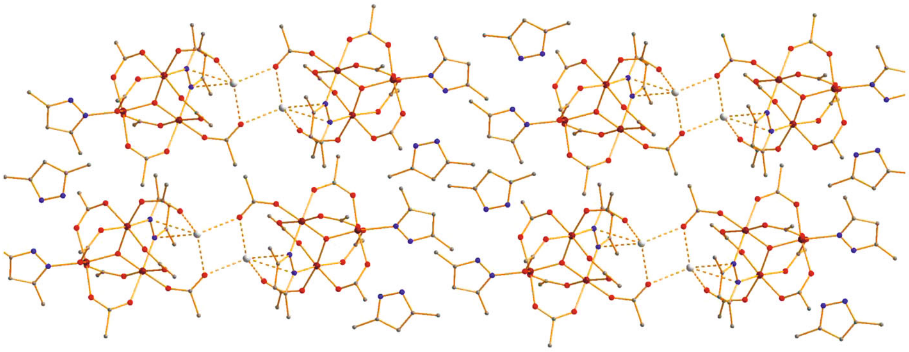

**Fig. 3.** Packing of the molecules of **I** in the crystal. For clarity, only the central carbon atoms are shown for the *tert*-butyl substituents of carboxylate anions. The iron atoms are shown in brown, the oxygen atoms are red, the nitrogen atoms are blue, and the carbon atoms are gray.

gen-bonded to the oxygen atom of the bridging pivalate anion (N(5)···O(1), 2.899(8) Å). The pyrrole nitrogen atoms are connected to the NH groups of the coordinated Dmpz (N(6)···N(2) 3.164(11) Å), which is in turn connected to the oxygen atom of bridging carboxylate group (N(2)···O(4), 2.830(9) Å) (Fig. 1).

In the crystal, molecules are localized and do not form noticeable contacts (Fig. 3).

No structurally characterized iron carboxylate complexes containing bridging pyrazolate anions are known. However, a number of compounds with other anions have been obtained in the reactions of iron(II, III) halides with alkali metals pyrazolates and by deprotonation of pyrazoles during the synthesis. For example, the reaction of Fe(NO)I with NaDmpz give the pyrazolate-bridged $Fe_2(\mu\text{-}Dmpz)_2(NO)_4$ dimer with Fe–N bond lengths of 2.009(5) Å and metal–metal distance of 3.3359(3) Å [17]. Deprotonation of unsubstituted pyrazole (HPz) with ferrocene for 5 days at 145°C in vacuum results in the formation of pyrazolate-bridged unsubstituted pyrazole polymer $[Fe(Pz)_2]_n$ (Fe–N 2.027(1) Å) [18]. The other synthesized compounds are trinuclear iron(III) complexes $Fe_3(\mu^3\text{-}O)(\mu\text{-}4\text{-}RPz)_6X_3$ (R = $NO_2$, X = Br [19], NCS [20], tetranuclear complexes $[LFe_3(\mu\text{-}3\text{-}PhPz)_3OFe][OTf]_2$ (L is the ligand based on the 1,3,5-triarylbenzene moiety [21]), and pyrazolate-bridged clusters containing a cubane metal core, $Fe_4(\mu^3\text{-}O)_4$, $Fe_8(\mu^4\text{-}O)_4(\mu\text{-}Pz)_{12}Cl_4$ [22] and $Fe_8(\mu^4\text{-}O)_4(\mu\text{-}4\text{-}RPz)_{12}X_4$, (X = Cl, Br; R = H, Me, Cl, $^t$Bu) [23–25].

It was shown that iron(II) carboxylates containing sterically congested 2,6-di(*para*-tolyl)benzoate and 2-phenylbenzoate anions react with HDmpz to give mononuclear and binuclear complexes with the Chinese lantern structure and coordinated pyrazole molecules. These complexes are considered as structural analogues of the active part of natural metalloenzymes [26–29].

It is also known that pyrazolate anions can act as $\eta^5,\pi$-ligands, for example, in $[Na(Dmpz)(Thf)]_4$, $[Na\{Al(Dmpz)_2Me_2\}]_n$ [28]; $Na(\eta^6\text{-}PhMe)\{Ln(3,5\text{-}{}^tBu_2Pz)_4\}$ (Ln = Tb, Ho), $[K(\eta^6\text{-}PhMe)\{Ln(3,5\text{-}{}^tBu_2Pz)_4\}] \cdot 2PhMe$ (Ln = La, Sm, Tb, Yb, Lu) (K–N, 2.83(1)–3.01(1); K–C, 3.07(1)–3.41(1) Å [30]; $K[(OC)_3Mn(\mu\text{-}Pz)_3Mn(CO)_3]$, in which the potassium cation occupies a bridging position and is connected to four bridging pyrazolate anions of two $Mn_2$ dimers (K–Pz center, 2.903–3.371 Å) [31]; and $(Thf)_6Ba_6(Dmpz)_8\{(OSiMe_2)_2O\}_2$ [32]. Note that the K–$\eta^5,\pi$-RPz distances in these complexes are quite in line with the distances in cluster **I**.

Thus, as a result of this study, we found that the reaction of aqueous iron(II) sulfate with potassium pivalate in the presence of $Et_3N$ as a deprotonating agent and HDmpz conducted under mild conditions gives, instead of the expected binuclear complex $M_2(\mu\text{-}Dmpz)_2(HDmpz)_2(OOC^tBu)_2$ analogous to zinc and cobalt complexes, an unusual cluster, $\{[Fe_3(\mu^3\text{-}O)(\mu\text{-}OOC^tBu)_4(OOC^tBu)_2(HDmpz)(\mu,\eta^5\text{-}Dmpz)(\mu\text{-}K)]_2 \cdot 2HDmpz\}$, as a final reaction product, which results from partial oxidation of the metal atoms linked to the strong donor pivalate anions.

## ACKNOWLEDGMENTS

XRD studies of the complexes were carried out at the Shared Use Center of the Institute of General and Inorganic Chemistry financed by the state assignment in the area of scientific research.

## FUNDING

This work was carried out in the framework of the state assignment of the Institute of General and Inorganic Chemistry in the area of scientific research.

## REFERENCES

1. Lippard, S.J. and Bergj, M., *Principles of Bioinorganic Chemistry*, Mill Valley: University Science Books, 1994.
2. Solomon, E.I., Sundaram, U.M., and Machonkin, T.E., *Chem. Rev.*, 1996, vol. 96, p. 2563. https://doi.org/10.1021/cr950046o
3. Dance, I.Z. and Lubitz, W., *Anorg. Allg. Chem.*, 2015, vol. 641, p. 91. https://doi.org/10.1002/zaac.201400120
4. Lubitz, W., Ogata, H., Rudiger, O., and Reijerse, E., *Chem. Rev.*, 2014, vol. 114, p. 4081. https://doi.org//10.1021/cr4005814
5. Kaim, W. and Rall, J., *J. Angew. Chem., Int. Ed.*, 1996, vol. 35, p. 43. https://doi.org/10.1002/anie.199600431
6. Holm, R.H., Kennepohl, P., and Solomon, E.I., *Chem. Rev.*, 1996, vol. 96, p. 2239. https://doi.org/0.1021/cr9500390
7. Eady, R.R., *Coord. Chem. Rev.*, 2003, p. 237. https://doi.org/10.1016/S0010-8545(02)00248-5
8. Baran, P., Boca, R., Chakraborty, I., et al., *Inorg. Chem.*, 2008, vol. 47, p. 645. https://doi.org/10.1021/ic7020337
9. Ruiter, G., De Thompson, N.B., and Lionetti, D., *J. Am. Chem. Soc.*, 2015, vol. 137, p. 14094. https://doi.org/10.1021/jacs.5b07397
10. Mehrotra, R.C. and Bohra, R., *Metal Carboxylates*, London: Acad., 1983, p. 396.
11. Cotton, F.A., Wilkincon, G., Murillo, C.A., and Bochmann, M., *Advanced Inorganic Chemistry*, New York: Wiley, Inc., 1999.
12. Kiskin, M.A. and Eremenko, I.L., *Russ. Chem. Rev.*, 2006, vol. 75, p. 559. https://doi.org/10.1070/RC2006v075n07ABEH003636
13. Nefedov, S.E., *Russ. J. Inorg. Chem.*, 2006, vol. 51, suppl. 1, p. S49. https://doi.org/10.1134/S0036023606130031
14. *SMART (control) and SAINT (integration) Software. Version 5.0*, Madison: Bruker AXS Inc., 1997.
15. *SAINT: Area-Detector Integration Sofware*, Madison: Bruker AXS Inc., 2012.
16. Sheldrick, G.M., *SADABS. Program for Scaling and Correction of Area Detector Data*, Göttingen (Germany): Univ. of Göttingen, 1997.
17. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.,* 2015, vol. 71, p. 3. https://doi.org/10.1107/S2053229614024218
18. Chong, K.S., Rettig, S.J., Storr, A., and Trotter, J., *Can. J. Chem.*, 1979, vol. 57, p. 3119. https://doi.org/10.1139/v79-509
19. Patrick, B.O., Reiff, W.M., Sanchez, V.A., et al., *Polyhedron*, 2001, vol. 20, p. 1577. https://doi.org/10.1016/S0277-5387(01)00657-X
20. Sameera, W.M.C., Pinero, D.M., Herchel, R., et al., *Eur. J. Inorg. Chem.*, 2012, p. 3500. https://doi.org/1002/ejic.201200206
21. Govor, E.V., Al-Ameed, K., Chakraborty, I., et al., *Angew. Chem., Int. Ed.*, 2017, vol. 56, p. 582. https://doi.org/10.1002/anie.201610534
22. Ruiter, G., De Thompson, N.B., Lionetti, D., and Agapie, T., *J. Am. Chem. Soc.*, 2015, vol. 137, p. 14094. doi.org/14094 10.1021/jacs.5b07397
23. Raptis, R.G., Georgakaki, I.P., and Hockless, D.C.R., *Angew. Chem., Int. Ed.*, 1999, vol. 38, p. 1632. https://doi.org/10.1002/(SICI)1521-3773(19990601)38:11<1632::AID-ANIE1632>3.0.CO;2-O
24. Chakraborty, I., Baran, P., Sanakis, Y., Simopoulos, A., et al., *Inorg. Chem.*, 2008, vol. 47, p. 11734. https://doi.org/10.1021/ic801459s
25. Baran, P., Boca, R., Chakraborty, I., et al., *Inorg. Chem.*, 2008, vol. 47, p. 645. https://doi.org/10.1021/ic7020337
26. Deutscher, J., Corona, T., Warm, K., et al., *Eur. J. Inorg. Chem.*, 2018, vol. 45, p. 4925. https://doi.org/10.1002/ejic.201800269
27. Sungho Yoon and Lippard, S.J., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 2666. https://doi.org/10.1021/ja031603o
28. Reisner, E., Telser, J., and Lippard, S.J., *Inorg. Chem.*, 2007, vol. 46, p. 10754. https://doi.org/10.1021/ic701663j
29. Cortes-Llamas, S., Velazquez-Carmona, M.-A., and Munoz-Hernandez, M.-A., *Inorg. Chem. Commun.*, 2005, vol. 8, p. 155. https://doi.org/10.1016/j.inoche.2004.11.028
30. Deacon, G.B., Delbridge, E.E., Evans, D.J., et al., *Chem.-Eur. J.*, 2004, vol. 10, p. 1193. https://doi.org/10.1002/chem.200305444
31. Morawitz, T., Zhang, F., Bolte, M., et al., *Organometallics*, 2008, vol. 27, p. 5067. https://doi.org/10.1021/om800504r
32. Steiner, A., Lawson, G.T., Walfort, B., et al., *Dalton Trans.*, 2001, p. 219. https://doi.org/10.1039/b009121i

*Translated by Z. Svitanko*