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New Approach to the Synthesis of Polynuclear Heterometallic Pivalates with Iron and Manganese Atoms

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Abstract—New hexanuclear Fe(III)–Mn(II, III) pivalates $[Fe_2^{III}Mn_4^{II}(O)_2(Piv)_{10}(HPiv)_4]$ (**I**) or $[Fe_4^{III}Mn_2^{III}(O)_2(Piv)_{12}(CH_2O_2)(HPiv)_2] \cdot Et_2O$ (**II**) are synthesized using the solid-state thermolysis of $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$ (90°C). Complexes **I** and **II** differ by the ratio of iron and manganese ions, which depends on the atmospheric composition during thermolysis. The structures of compounds **I** and **II** are determined by X-ray diffraction studies. According to the parameters of the Mössbauer spectrum, complex **I** contains the Fe^{3+} ions in the high-spin state in the octahedral environment of oxygen atoms.

Keywords: heterometallic carboxylate complexes, iron(III), manganese(II, III), crystal structure, Mössbauer spectroscopy, solid-state thermolysis

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INTRODUCTION

Pivalate (trimethylacetate) complexes with 3*d*-metal atoms attract attention of researchers due to high solubility in organic solvents, providing their possible use as precursors in technological processes for the production of diverse functional materials (for example, simple and complex oxides) [1, 2]. In addition, taking into account high polyfunctionality of carboxylate anions as organic ligands linked to metal centers, one can find a possibility of their additional use for growing metal frameworks of polynuclear structures staring from mono- or polynuclear carboxylate complex blocks [3–5]. This is especially important in the case of heterometallic complexes where the structure contains metal ions with different electronic and spatial characteristics. In this situation, one can more or less purposefully construct a future molecular architecture formed due to metal framework growing and also to predict the properties (catalytic, sorption, optical, magnetic, and/or electroconducting) [6–12]) of new molecules. Concerning the ways for the formation of carboxylate clusters with unusual electronic characteristics (for example, magnetic characteristics), it is important to find approaches to the assembling of heteronuclear complex blocks with high-spin metal ions, which can be used further for the construction of larger molecules suitable for the preparation of magnetic devices, for example, high density memory modules or magnetic sensors [13–15].

Therefore, we noticed the ability of manganese ions to manifest several stable oxidation states in the carboxylate complexes, which provides possibilities for the preparation of basically different compounds by the variation of temperature and oxidation–reduction conditions. The most part of publications is devoted to the trinuclear carboxylate complexes of the general formula $[Mn_3O(O_2CR)_6(L)_3]^z$ (z = 1+, 0) [16–24] with Mn^{2+} and Mn^{3+} ions. The heterometallic systems, including the {Fe–Mn} complexes, are less studied [1, 14, 25]. Although the listed carboxylates can undoubtedly be used as blocks for the formation of new clusters, in this work we propose a new approach to the synthesis of the starting heteronuclear pivalate complex blocks suitable for the preparation of complicated heterometallic {Fe–Mn} architectures with unusual electronic characteristics.

EXPERIMENTAL

The complexes were synthesized using the following commercial reagents and solvents without additional purification: pivalic acid (HPiv) (Merck), KOH (analytical grade), $Fe(NO_3)_3 \cdot 9H_2O$ (Khimmed, high-purity grade), $Mn(NO_3)_2 \cdot 4H_2O$ (Khimmed,

high-purity grade), diethyl ether (analytical grade), acetone (analytical grade), and acetonitrile (Khimmed, special purity grade). Anaerobic thermolysis was carried out in an argon flow (Ar, >99.998%; O_2, 0.0002%; N_2, <0.001%; H_2O, <0.0003%; CH_4, <0.0001%). The starting trinuclear complex $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$ was synthesized using a described procedure [1] and characterized by the IR spectra and chemical analysis data.

IR spectra were recorded on a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer using the attenuated total reflection (ATR) method in a frequency range of 400–4000 cm^{-1}.

Elemental analysis was carried out on a Carlo Erba EA 1108 automated C,H,N,S-analyzer combined with mass spectrometry with inductively-coupled plasma (ICP) on an Agilent 7500ce instrument (Agilent Technologies Inc., USA).

Syntheses of $[Fe_2^{III}Mn_4^{II}(O)_2(Piv)_{10}(HPiv)_4]$ (I) and $[Fe_4^{III}Mn_2^{III}(O)_2(Piv)_{12}(CH_2O_2)(HPiv)_2] \cdot (C_2H_5)_2O$ (II). A weighed sample of the brown powder of $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$ (0.331 g) was kept in a Schlenk flask at 90°C in an argon atmosphere for 120 min, shaking the contents at intervals of 30 min. A portion of the tawny powder obtained by thermolysis (100 mg) was recrystallized from acetone (25 mL) at room temperature. The formed red-brown crystals of complex **I** were washed with cold acetonitrile (~7°C) and dried in air. The yield was 0.046 g (46%).

According to the ICP data (mg/mL), Fe : Mn = 1 : 2.

For $C_{30}H_{54}O_{13}Mn_4Fe_2$		
anal. calcd., %:	C, 47.15;	H, 7.35.
Found, %:	C, 47.23;	H, 7.13.

IR (ν, cm^{-1}): 2962 m, 2930 w, 2870 w, 1697 m, 1586 vs, 1568 vs, 1481 vs, 1459 m, 1412 vs, 1379 s, 1358 vs, 1318 m, 1226 vs, 1240 s, 1031w, 938 w, 896 m, 872 m, 787 m, 762 w, 602 vs, 590 vs, 555 s, 534 s, 435 vs, 419 vs.

Another weighed sample of the brown powder of $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$ (1.19 g) was kept in a porcelain beaker at 90°C in air for 120 min, shaking the contents at an interval of 30 min. A portion of the brown thermolyzed powder (100 mg) was dissolved in diethyl ether (30 mL) to obtain a brown solution, which was kept for 48 h at ~7°C. The formed brown crystals of complex **II** were washed with cold acetonitrile (~7°C) and dried in air. The yield was 0.025 g (25%).

According to the ICP data (mg/mL), Fe : Mn = 2 : 1.

IR (ν, cm^{-1}): 2963 m, 2930 w, 1698 s, 1593 m, 1544 s, 1482 vs, 1457 m, 1419 vs, 1378 s, 1357 vs, 1227 vs, 1149 m, 1032 m, 961 m, 899 s, 787 s, 651 m, 587 vs, 516 vs, 436 vs, 420 vs.

X-ray diffraction analyses for the crystals of complexes **I** and **II** were carried out on a Bruker Apex II diffractometer (CCD detector, MoK_α, λ = 0.71073 Å, graphite monochromator) [26]. A semiempirical absorption correction (T_{min}/T_{max} = 0.762/0.932) was applied for complex **I** [27]. The structures of complexes **I** and **II** were solved by direct methods and refined in the full-matrix least-squares anisotropic approximation (SHELXL-2014/7) [27]. The hydrogen atoms in the ligands were calculated geometrically and refined in the riding model. The metal atoms in the M_6 framework in a molecule of complex **II** were refined as iron atoms (according to the ICP data, the Fe : Mn ratio is 2 : 1). The *tert*-butyl substituents at the carboxylate group in compound **II** were determined taking into account disordering. The positions of the methyl carbon atoms in the $\{CMe_3\}$ fragments (the population of the C(32) in **II** is 0.459(13) and 0.541(13)) and the positions of the carboxylate groups in two disordered HPiv ligands in **II** were localized from the difference Fourier synthesis (the population of C(61) was 0.488(9) and 0.512(9) and that of C(66) was 0.535(11) and 0.465(11)).

The crystallographic parameters and structure refinement details for complexes **I** and **II** are presented in Table 1. Selected bond lengths and interatomic distances are given in Table 2. The full array of X-ray diffraction results was deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC no. 1507877 (**I**) and 1507878 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

The X-ray phase analyses for both samples were carried out on a Bruker D8 Advance instrument (CuK_α, λ = 1.54 Å, Ni filter, LYNXEYE detector).

Mössbauer spectroscopy for compound **I** ^{57}Fe was conducted on a Wissel electrodynamic type spectrometer (Germany) at 300 K. The accuracy of temperature maintenance was not lower than ±0.1 K. The studied sample contained "natural" iron, the content of the ^{57}Fe isotope in which did not exceed 3 wt % (owing to this, the value of the Mössbauer effect did not exceed 2%). The Mössbauer radiation source was ^{57}Co(Rh) with an activity of 1.1 GBq. Isomeric shifts were counted from the center of the magnetic hyperfine structure of metallic iron. The spectrum was processed using the standard calculation and simulation programs for the Mössbauer transition 3/2 → 1/2. The complex processing of the Mössbauer spectrum was performed by least squares using the LRT (Semenov Institute of Chemical Physics, Russian Academy of Sciences) and WINNORMOS (Germany) programs.

RESULTS AND DISCUSSION

One of the methods for metal framework modification in polynuclear structures is the partial or complete removal of neutral molecules from the complex resulting in the formation of coordinately unsaturated

Table 1. Crystallographic data and structure refinement details for compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{70}H_{130}O_{30}Mn_4Fe_2$	$C_{75}H_{140}O_{33}Mn_2Fe_4$
M, g/mol	1783.23	1904.96
T, K	150(2)	160(2)
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
Crystal size, mm	0.32 × 0.17 × 0.08	0.32 × 0.18 × 0.07
Crystal color	Red-brown	Brown
a, Å	26.502(2)	14.129(2)
b, Å	24.862(2)	19.447(3)
c, Å	28.265(2)	19.474(3)
α, deg	90	77.846(2)
β, deg	90	77.767(2)
γ, deg	90	89.859(2)
V, Å^3	18623(2)	5107.2(11)
Z	8	2
ρ_{calcd}, g/cm^3	1.272	1.239
μ, mm^{-1}	0.899	0.899
F(000)	7536	2020
Data collection range over θ, deg	2.10–23.26	1.07–25.24
Ranges of reflection indices	$-29 \le h \le 29$, $-27 \le k \le 27$, $-31 \le l \le 31$	$-17 \le h \le 17$, $-23 \le k \le 23$, $-23 \le l \le 23$
Number of measured reflections	97885	40588
Number of independent reflections (R_{int})	13 286 (0.125)	19 212 (0.121)
Number of reflections with $I > 2\sigma(I)$	6641	7593
Refinement variables	955	1036
GOOF	1.180	0.946
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.126$, $wR_2 = 0.287$	$R_1 = 0.067$, $wR_2 = 0.150$
R factors for all reflections	$R_1 = 0.214$, $wR_2 = 0.363$	$R_1 = 0.169$, $wR_2 = 0.190$
Residual electron density (min/max), e/Å^3	–0.954/4.935	–0.709/1.129

Table 2. Selected bond lengths and interatomic distances (Å) for complexes **I** and **II**

Distance	Metal	*d*, Å	Metal	*d*, Å
		I		**II**
M–O($\mu_{3/4}$-O)	M = Fe	1.885(6)–1.894(6)	M = Fe, Mn	1.852(4)–1.965(5)
	M = Mn	2.145(6)–2.165(6)		
M–O(Piv)	M = Mn	2.081(8)–2.317(9)	M = Fe, Mn	1.981(5)–2.059(5)
	M = Fe	1.935(7)–2.267(8)		
M–O(O_2CH_2)			M = Fe, Mn	1.978(4)–2.008(5)
M–O(HPiv)	M = Mn	2.229(9)–2.243(8)	M = Fe, Mn	2.180(5), 2.167(14)
M···M	Fe···Fe	2.826(2)	M = Fe, Mn	3.2774(3)–3.5946(4)
	Mn···Mn	3.710(2), 3.729(2)		
	Fe···Mn	3.116(2)–3.477(2)		

metal centers. As a rule, this route is efficient when small polynuclear molecules or coordination polymers containing neutral organic ligands serve as the stating blocks. In our case, we used this approach for the thermolysis of solid $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$ [1]. The thermolysis was carried out in air and in an inert atmosphere at 90°C to remove solvate and coordinated HPiv from the starting amorphous compound. The course of thermolysis was monitored gravimetrically and using IR spectroscopy by the detection of the disappearance of the characteristic bands at 1700–1200 cm^{-1} corresponding to ν(–OC=O) of the carboxylate groups (Fig. 1). As a result, the weight of desorbed HPiv was 0.09/0.34 g (27.5/28.7%), and for $HPiv_{calcd}$ 28.1%.

The crystals of the complexes with different Fe : Mn ratios were isolated by the crystallization of the substances obtained by the thermal treatment in an argon atmosphere and in air from acetone and diethyl ether, respectively. The composition of complex **I** obtained by thermolysis in argon and crystallization from acetone corresponds to the formula $[Fe_2^{III}Mn_4^{II}(O)_2(Piv)_{10}(HPiv)_4]$, and that of complex **II** obtained by thermolysis in air and crystallization from ether is $[Fe_4^{III}Mn_2^{III}(O)_2(Piv)_{12}(O_2CH_2)(HPiv)_2] \cdot Et_2O$. The both metal atoms in the latter turned out to be trivalent. The Fe : Mn ratio in complex **II** was confirmed by the ICP analysis to metals (see Experimental).

Complex **II** in which the manganese(II) ion (also present in complex **I**) is oxidized by air oxygen to Mn(III) is formed due to the difference in the standard potentials

$$Mn^{2+} - \bar{e} = Mn^{3+} (E^0 = -1.51 \text{ V}) \text{ [28]},$$

$$O_2 + 4H^+ + 4\bar{e} = 2H_2O (E^0 = 1.23 \text{ V}), \Delta E = 2.74 \text{ V}$$

(the reaction proceeds spontaneously).

In addition, the dianion $[O_2CH_2]^{2-}$ stabilized by binding with four metal atoms in the cluster framework is unexpectedly formed in the oxidation product. As a result, according to the X-ray diffraction data, complexes **I** and **II** have the molecular structures (Table 1, Fig. 2).

The metal framework of the complex is presented by the $\{Fe_2Mn_4O_2\}$ fragment (two tetrahedra with the common Fe(1)Fe(2) side (Fig. 2a) in which the central Fe(1) and Fe(2) atoms are linked to each other by four peripheral manganese(II) atoms of the μ_4-bridging oxo groups. The metal atoms are additionally bound by ten μ_2- and μ_3-bridging carboxylate groups to form a hexanuclear complex similar to the known compounds $[M'_2M''_4O_2(O_2CR)_{10}L_4]$ (M', M'' = Mn(II/III) [29, 30]; M' = Ni, Co; M'' = Mn(III)). In addition, four manganese(II) atoms coordinate one terminal HPiv molecule each, thus completing the octahedral environment of the metal ions.

In complex **II**, unlike complex **I**, the metal framework can be presented as two triangles $\{Fe_2Mn\}$ linked

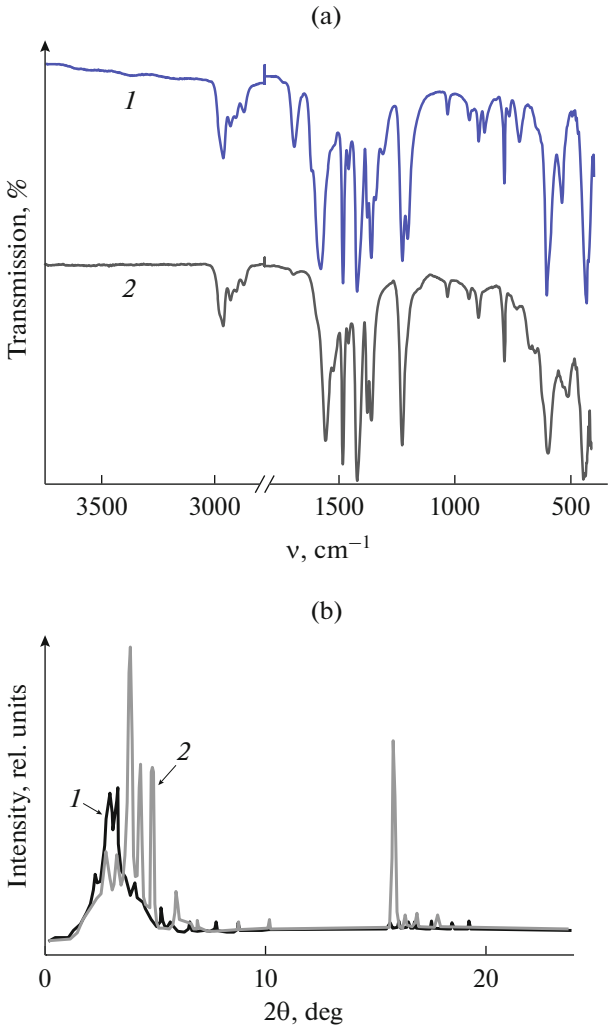


Fig. 1. (a) IR spectra of (*1*) complex $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$ and (*2*) the product formed after the thermal treatment in an Ar atmosphere; (b) the powder diffraction patterns for the thermolysis products of $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$: in (*1*) Ar and (*2*) air.

to each other by two Piv^- ions and one $CH_2O_2^{2-}$ dianion at one of the sides (Fig. 2b). We failed to separate the positions of the Mn and Fe atoms on the basis of the X-ray diffraction data, in spite of the fact that the Mn^{3+} ion should be characterized by the Jahn–Teller distortion. This situation is possible for the disordered arrangement of the iron(III) and manganese(III) ions localized in the corresponding positions with the populations 2/3 and 1/3, respectively.

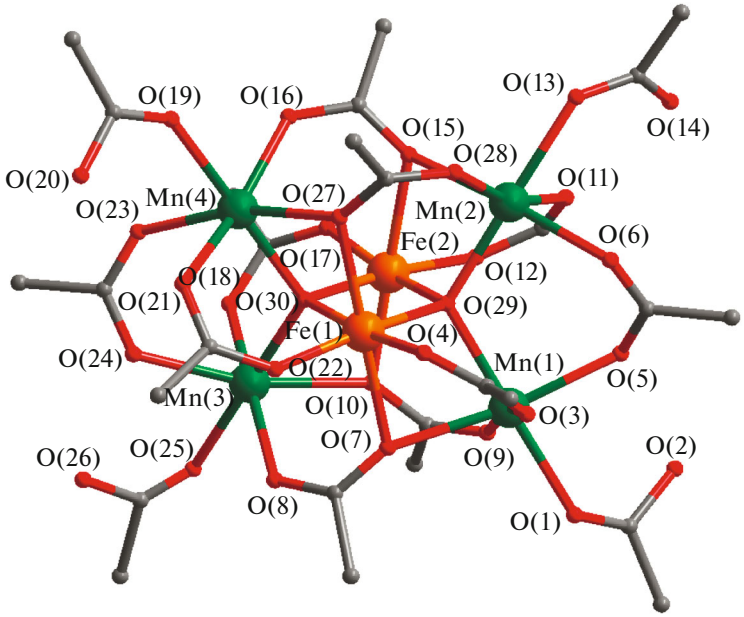
Complex **II** is a formal analog of the known homometallic complexes of the general formula $[M_6(O)_2(O_2CR)_{12}(O_2CH_2)L_2]$ (M = Fe, Mn) [31–34].

The quadrupole Mössbauer spectrum was studied at 300 K in the zero magnetic field for the solid sample of complex **I**. The spectrum represents a single doublet (Fig. 3), possibly indicating the structural equivalence of all iron atoms in the molecule.

The values of isomeric shifts (δ) and quadrupole splittings (Δ) (Table 3) make it possible to conclude that the complex contains high-spin Fe^{3+} ions in the octahedral environment of the O atoms, which is consistent with the X-ray diffraction data. The possibility for iron(II) ions to be in complex **I** is excluded. The values of δ and Δ approximately correspond to the values for other Fe(III) carboxylate complexes studied earlier [35–37] (δ 0.43–0.47 mm/s, Δ 0.62–0.68 mm/s).

Thus, it was shown for the trinuclear complex $[Fe_2Mn(O)(Piv)_6(HPiv)_3]$ that the metal framework can be grown using solid-state thermal reactions. The variation of the atmosphere of the thermal process gives different results: the growth of the metal framework in an inert atmosphere does not change the electron state of the metal centers in the formed hexanuclear complex **I**, whereas an air atmosphere leads to the oxidation of the manganese ions in the formed complex **II** isolated as a solvate with Et_2O after recrystallization from diethyl ether.

(a)



(b)

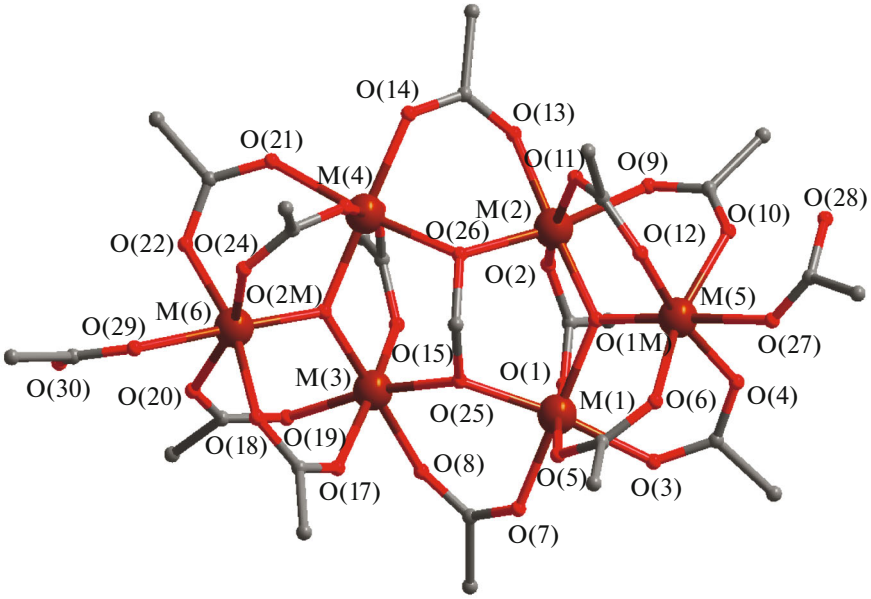


Fig. 2. Molecular structures of compounds (a) **I** and (b) **II** (M(i) = 2/3Fe and 1/3Mn, i = 1–6); (hydrogen atoms, methyl groups at the carboxylate ligands, and solvate molecules are omitted).

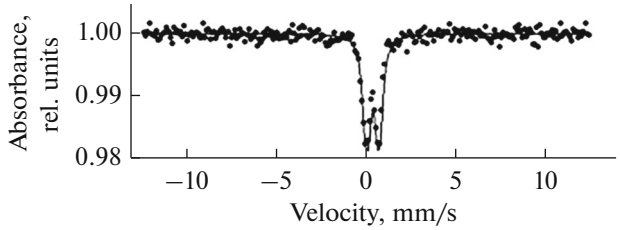


Fig. 3. Mössbauer spectrum of a solid sample of compound **I** (T = 300 K).

Table 3. Parameters of the Fe(III) forms in complex **I***

Complex	*T*, K	Form of Fe	δ	Δ	Γ	*A*, ±0.05	Literature
			±0.03 mm/s				
I	300	Fe^{3+} (paramagnetic)	0.42	0.67	0.44	1	This work
$[Fe_2(OH)_{0.3}(H_2O)_{1.7}(Btc)_{4/3}]Cl_{1.7}$	300	Fe^{3+} (paramagnetic)	0.43	0.68			[35]
$[Fe_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 5H_2O$	300	Fe^{3+} (paramagnetic)	0.40	0.61			[36]
$[Fe_3O(CH_3COO)_6(H_2O)_3][FeCl_4] \cdot 2CH_3COOH$	300	Fe^{3+} (paramagnetic)	0.41	0.53	0.27		[37]

* δ is the isomeric shift relative to α-Fe, Δ is the quadrupole splitting or quadrupole shift, Γ is the linewidth, and *A* is the relative content.

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REFERENCES

1. Abdulwahab, K.O., Malik, M.A., O'Brien, P., et al., *Chem. Mater.*, 2014, vol. 26, p. 999.
2. Long, J.R., *Molecular Cluster Magnets*, Yang P., Ed., Hong Kong: World Scientific, 2003, p. 291.
3. Burkovskaya, N.P., Nikiforova, M.E., Kiskin, M.A., et al., *Polyhedron*, 2012, vol. 35, p. 116.
4. Dobrokhotova, Zh.V., Fomina, I.G., Kiskin, M.A., et al., *Russ. Chem. Bull.*, 2006, vol. 55, p. 256.
5. Fomina, I.G., Aleksandrov, G.G., Dobrokhotova, Zh.V., et al., *Russ. Chem. Bull.*, 2006, vol. 55, p. 1909.
6. Rashad, M.M. and Fouad, O.A., *Mater. Chem. Phys.*, 2005, vol. 94, p. 365.
7. Karunananda, M.K., Vazquez, F.X., Alp, E.E., et al., *Dalton Trans.*, 2014, vol. 43, p. 13661.
8. Veith, M., Haas, M., and Huch, V., *Chem. Mater.*, 2005, vol. 17, p. 95.
9. Godbole, R.V., Rao, P., Alegaonkar, P.S., and Bhagwat, S., *Mater. Chem. Phys.*, 2015, vol. 161, p. 135.
10. Yeary, L.W., Moon, J.W., Rawn, C.J., et al., *J. Magn. Magn. Mater.*, 2011, vol. 323, p. 3043.
11. Naseri, M.G., Saion, E.B., Hashim, M., et al., *Solid State Commun.*, 2011, vol. 151, p. 1031.
12. Doungmene, F., Aparicio, P.A., Ntienoue, J., et al., *Electrochim. Acta*, 2014, vol. 125, p. 674.
13. Dulcevscaia, G.M., Filippova, I.G., Speldrich, M., et al., *Inorg. Chem.*, 2012, vol. 51, no. 9, p. 5110.
14. Kim, J. and Cho, H., *Inorg. Chem. Commun.*, 2004, vol. 7, p. 122.
15. Tavakkoli, H., Arezoo Ghaemi, A., and Mohave, F., *Int. J. Sci. Res. Knowledge*, 2013, vol. 1, no. 7, p. 182.
16. Uemura, S., Spencer, A., and Wilkinson, G., *J. Chem. Soc., Dalton Trans.*, 1973, p. 2565.
17. Baikie, A.R.E., Hursthouse, M.B., New, D.B., and Thornton, P., *J. Chem. Soc., Chem. Commun.*, 1978, p. 62.
18. Baikie, A.R.E., Hursthouse, M.B., and New, D.B., et al, *J. Chem. Soc., Chem. Commun.*, 1980, p. 684.
19. Vincent, J.B., Chang, H.R., Folting, K., et al., *J. Am. Chem. Soc.*, 1987, vol. 109, p. 5703.
20. McCusker, J.K., Jang, H.G., Wang, S., et al., *Inorg. Chem.*, 1992, vol. 31, p. 1874.
21. Li, J., Yang, S., Zhang, F., et al., *Inorg. Chim. Acta*, 1999, vol. 294, p. 109.
22. Canada-Vilalta, C., Huffman, J.C., Streib, W.E., et al., *Polyhedron*, 2001, vol. 20, p. 1375.
23. Li, J., Zhang, F., Shi, Q., et al., *Inorg. Chem. Commun.*, 2002, vol. 5, p. 51.
24. Kim, J. and Cho, H., *Inorg. Chem. Commun.*, 2004, vol. 7, p. 122.
25. Blacman, A.G., Huffman, J.C., Lobkovsky, E.B., and Christou, G., *Polyhedron*, 1992, vol. 11, no. 2, p. 251.
26. *SMART (control) and SAINT (integration) Software. Version 5.0*, Madison: Bruker AXS Inc.,1997.
27. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
28. Rabinovich, V.A. and Khavin, Z.Ya. *Kratkii khimicheskii spravochnik* (Brief Chemist's Handbook), Leningrad: Khimiya, 1977.
29. Gavrilenko, K.S., Punin, S.V., Cador, O., et al., *Inorg. Chem.*, 2005, vol. 44, p. 5903.
30. Kar, P., Haldar, R., Gomez-García, C.J., and Ghosh, A., *Inorg. Chem.*, 2012, vol. 51, p. 4265.
31. Fursova, E.Yu., Romanenko, G.V., and Ovcharenko, V.I., *Russ. Chem. Bull.*, 2005, vol. 54, p. 811.
32. Baca, S.G., Secker, T., Mikosch, A., et al., *Inorg. Chem.*, 2013, vol. 52, p. 4154.
33. Chakov, N.E., Zakharov, L.N., Rheingold, A.L., et al., *Inorg. Chem.*, 2005, vol. 44, p. 4555.
34. Murugesu, M., Abboud, Kh.A., and Christou, G., *Polyhedron*, 2004, vol. 23, p. 2779.
35. Sotnik, S.A., Kolotilov, S.V., Kiskin, M.A., et al., *Russ. Chem. Bull.*, 2014, vol. 63, p. 862.
36. Rumbold, B.D. and Wilson, G.V.H., *J. Phys. Chem. Solids*, 1973, vol. 34, p. 1887.
37. Shova, S.G., Cadelnic, I.G., Gdaniec, M., et al., *J. Struct. Chem.*, 1998, vol. 39, no. 5, p. 747.

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