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Isomers in the chemistry of iron coordination compounds

Review Article

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Abstract: The coordination chemistry of iron covers a wide field, as shown by a survey covering the crystallographic and structural data of almost one thousand and three hundred coordination complexes. About 6.7% of these complexes exist as isomers and are summarized in this review. Included are distortion (96.6%) and *cis – trans* (3.4%) isomers. These are discussed in terms of the coordination about the iron atom, bond length and interbond angles. Distortion isomers, differing only by degree of distortion in Fe-L, Fe-L-Fe and L-Fe-L parameters, are the most common. Iron is found in the oxidation states zero, +2 and +3 of which +3 is most common. The stereochemistry around iron centers are tetrahedral, five – coordinated (mostly trigonal – bipyramid) and six – coordinated. The most common ligands have O and N donor sites.

Keywords: *Iron • Complexes • Distortion • Cis – trans • Isomers*

1. Introduction

Systematic studies in the field of stereoselectivity of coordination compounds over the last 50 years have become of increasing interest. Stereoselectivity in coordination compounds is very often related to important stereospecificity of biological systems, catalysis and stereochemical effects in technical processes. Isomers can be broadly classed into two major categories, structural and stereoisomers. The former can be divided into ionization, hydrate, coordination, linkage, and polymerization sub – categories, and the latter can be divided into geometric (cis – trans, fac – mer), optical and distortion isomerism.

Iron exists in a wide range of oxidation states from – 2 to + 4 and +6 including mixed oxidation states (average Fe(II) Fe(III) or Fe(III) Fe(IV)). Of these particularly in six coordinate examples + 2 and + 3 oxidation states are the most common. The huge area, of iron coordination chemistry has been surveyed [1,2] with almost one hundred twenty isomeric examples noted. In this review we analyze and classify these examples to show that stereoisomers are more common than structural isomers. The aim of this presentation is to discuss the factors which could lead to a better understanding of stereochemical interaction within the coordination sphere of mono – and oligomeric iron coordination compounds, and to examine some cooperative effects between isomeric types.

2. Distortion Isomerism

The coexistence of two or more species differing only by degree of distortion of M-L bond distances and L-M-L bond angles is typical of the general class of distortion isomers [3].There are almost one hundred and twenty such examples in the chemistry of iron coordination compounds. The iron oxidation states in these isomers are found in the oxidation states of zero, + 1, + 2, and +3 (the most common).

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2.1. Monomeric complexes

2.1.1. Isomeric forms

There are three examples [4–8] which exist in two isomeric forms the crystallographic parameters of which are given in Table 1. Dark red $[Fe^{II}\{\eta^6\text{-}(pp)_2H\}]PF_6 \bullet 2\,H_2O$ which exists in two crystal classes orthorhombic [4] and monoclinic [4] consists in well separated $[Fe^{II}\{\eta^6\text{-}(pp)_2H\}]^+$ cations, PF_6^- anions and water molecules. The hexadentate $(pp)_2H$ ligand forms low – spin derivatives with a FeN_6 core with the mean Fe – N bond distances of 1.95 Å and the mean five – membered metallocyclic rings of 82.0 and 81.2°, respectively.

Two isomeric forms of black $[Fe^{III}\{\eta^2\text{–}(CH_2)_4NCS_2\}_3]$ are homo – monoclinic [5,6]. In both three homo – bidentate – S,S' ligands created around each iron (III) atom a pseudo – octahedral arrangement (FeS_6). The mean Fe – S bond distances are 2.456(2) Å [5] and 2.41(1) Å [6]. The mean four – membered metallocyclic rings are 72.6 and 74.4°, respectively.

Two isomeric forms of purple $Fe^{III}(\eta^4\text{-tpp})Cl$ differ by crystal class, one is tetragonal [7] and the other is monoclinic [8]. The iron(III) atom in the former exists in low spin (S = 0) state, while in the latter it is in high spin (S = 2). In both of the isomers a square pyramidal environment around iron(III) is built up from one unidentate chlorine atom (at the apex) and one tetradentate tpp – N_4 ligand (in the plane).

The displacement of the iron(III) atom from the basal plane of the square plane N_4 donor atoms toward the apical chloride atom is 0.383(5) and 0.49 Å, respectively. The sum of all five (Fe-N (4x) plus Fe-Cl (1x)) bond distances are 10.388 Å [7] and 10.491 Å [8]. This indicates that the former isomer is somewhat more thronged than the latter.

2.1.2. Independent molecules

There are fifty five derivatives which contain two crystallographically independent molecules and another three derivatives which contain three such molecules. Their crystallographic and structural parameters are given in Table 2. Yellow monoclinic $Fe^0(Bu^tNC)_5$ [9] is the only example of Fe(0) which contains two crystallographically independent molecules. Five unidentate Bu^tNC ligands created around each iron(0) a trigonal bipyramidal coordination (FeC_5) with the mean Fe-C_{eq} and Fe-C_{ax} bond distances (molecule 1 *vs.* molecule 2) of 1.813 and 1.824 Å *vs.* 1.825 and 1.835 Å.

There are sixteen iron(II) derivatives (Table 2). Structure of deep red derivative [10] consists of well separated $sacsac^+$ cations and $[FeCl_4]^{2-}$. Four unidentate chlorine atoms form around each iron(II) atom a tetrahedral arrangement with the mean Fe-Cl bond distances of 2.3213 Å (molecule 1) and 2.315 Å (molecule 2). The maximum deviation of Cl-Fe-Cl bond angles from the ideal tetrahedral angle (109.5°) are 6.3° and 6.6°, which indicates that the latter molecule is somewhat more distorted than the former.

In lavender $Fe^{II}Cl_2(\eta^2\text{-dppe})$ [11] two chlorine atoms and homo – bidentate dippe – P,P' ligand created a tetrahedral environment around each iron(II) atom

Table 1. Crystallographic and structural data for monomeric iron coordination compounds – distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	L – Fe – L [°]	Ref.
$[Fe^{II}\{\eta^6\text{-}(pp)_2H\}]PF_6 \bullet 2H_2O$ (dark red)	or Pbcm 4	9.420(4) 16.634(6) 21.894(4)		FeN_6	N[b]1.95(2,6)	N,N[b] 82.0(1,2)[c] 163(1)	4
$[Fe^{II}\{\eta^6\text{-}(pp)_2H\}]PF_6 \bullet 2H_2O$ (dark red)	m P2/c 4	13.350(6) 9.338(5) 16.752(9)	126.73(6)	FeN_6	N 1.953(5,49)	N,N 81.2(4,9)[c] 162.3(4)	4
$[Fe^{II}\{\eta^2\text{-}(CH_2)_4NCS_2\}_3]$ (black)	m $P2_1/a$ 4	18.033(6) 9.398(2) 13.176(6)	100.80(3)	FeS_6	S 2.456(2,25)	S,S 72.6(1,1)[d]	5
$[Fe^{II}\{\eta^2\text{-}(CH_2)_4NCS_2\}_3]$ (black)	m $P2_1/n$ 4	16.23(4) 14.53(2) 10.22(3)	90.3(4)	FeS_6	S 2.41(1,3)	S,S 74.4(3,8)[d] 96.2(3,10.6) 161.0(3,3.3)	6
$[Fe^{III}\{\eta^4\text{-tpp})Cl$ (purple)	tg I4/m 2	13.53 9.82		FeN_4Cl 0.383(5)	N_{eq} 2.049(9,0) Cl_{ap} 2.192(12)	not given	7
$[Fe^{III}\{\eta^4\text{-tpp})Cl$ (deep purple)	m $P2_1/n$ 4	10.254(2) 15.969(3) 20.810(4)	90.48(2)	FeN_4Cl 0.49	N_{eq} 2.070(3,10) Cl_{ap} 2.211(1)	N,N 86.8(1,4)[c] 152.6(1,8) N,Cl 103.7 (1,1.0)	8

[a] *Where more than one chemically equivalent distance or angle is present the mean value is tabulated. The first member in parenthesis is the e.s.d. , and the second is the maximum deviation from the mean*
[b] *The chemical identity of the coordinated atom or ligand is specified in these columns*
[c] *Five-membered metallocyclic ring*
[d] *Four-membered metalocyclic ring*

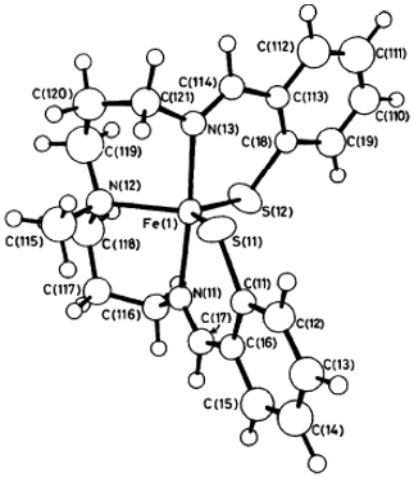

Figure 1. Structure of $[Fe^{II}(\eta^5\text{-tsalmah})]$ [15]

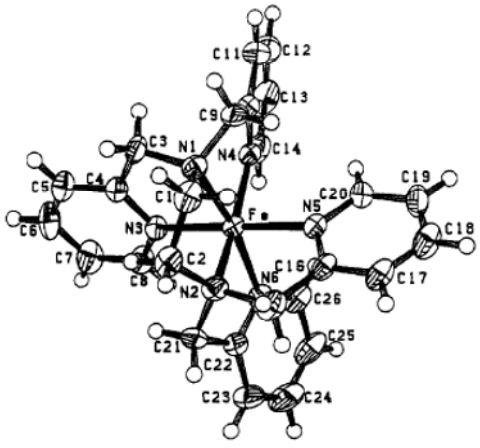

Figure 2. Structure of $[Fe^{II}(\eta^6\text{-tpen})]^{2+}$ [22]

($FeCl_2P_2$). The mean Fe-Cl and Fe-P bond distances (molecule 1 *vs.* molecule 2) are 2.23 and 2.47 Å *vs.* 2.25 and 2.44 Å. The Cl-Fe-Cl, P-Fe-P and Cl-Fe-P (mean) bond angles are 118.0(4), 83.7(3) and 112.5(5)° *vs.* 116.2(4), 84.0(3) and 113.1(4)° which indicates that the former is somewhat more distorted than the latter.

In pale yellow $[Fe^{II}(\eta^2\text{-opdp})_2I]\bullet 1.85(CH_2Cl_2)$ [12] a pair of homo – bidentate opdp – P, P' ligands occupy a square plane and iodine atom (at apex) complete a square pyramidal arrangement around each iron(II) atom (FeP_4I). The displacement of Fe(II) atom from the basal plane (P_4) atoms towards the apical iodine atom is 0.2 Å. The mean Fe-P and Fe-I bond distances (molecule 1 *vs.* molecule 2) are 2.336 and 2.632 Å *vs.* 2.351 and 2.646 Å. The mean five – membered P-Fe-P bond angles are 80.5 and 80.2°.

In $[Fe^{II}(\eta^4\text{-time})Cl]Cl\bullet 0.5MeOH\bullet 0.5H_2O$ [13] each iron(II) has a trigonal bipyramidal environment. Tetradentate N_4 donor atoms ligand span trigonal plane by two N donor atoms and remaining two N donor atoms occupy apical positions. One unidentate chloride atom completes the trigonal plane (FeN_4Cl). The sum of all five (Fe-N (×4) plus Fe-Cl (×1)) bond distances are 10.886 Å (molecule 1) and 10.797 Å (molecule 2). The N_{eq}-Fe-N_{eq} and N_{ax}-Fe-N_{ax} bond angles are 116.9(1) and 165.2(1)° (molecule 1) and 117.7(2) and 168.8(1)° (molecule 2). The mean N_{eq}- Fe-Cl_{eq} and N_{ax}-Fe-Cl_{eq} bond angles are 108.9 and 109.0° in the former and 105.8 and 109.6° in the latter. This indicates that the former is somewhat more distorted than the latter.

Structure of green derivative [14] consists of well separated $[Fe^{II}(\eta^4\text{-P4})Br]^+$ cation, BPh_4^- anion and CH_2Cl_2 molecule. In complex cation, each Fe(II) atom has a trigonal bipyramidal arrangement, two P atoms of tetradentate P_4 ligand with bromide atom form a trigonal plane and remaining two P atoms of the P_4 ligand occupied an axial positions. The sum of (Fe-N (x4) plus Fe-Br) bond distances (molecule 1 *vs.* molecule 2) are 11.305 *vs.* 11.146 Å. The former is somewhat less crowded than the latter.

In deep red $[Fe^{II}(\eta^5\text{-tsalmah})]$ [15] pentadentate N_3S_2 tsalmah ligand forms around iron(II) a trigonal bipyramidal arrangement (Fig. 1). One N atom together with two S atoms created a trigonal plane and remaining two N atoms occupies an axial position. Noticeably, the Fe-N_{eq} bond distances of 2.20(1) Å (molecule 1) and 2.23(2) Å (molecule 2) are longer than the Fe-N_{ax} bond distances, with the mean values of 2.13(2) and 2.14(2) Å, respectively. The mean Fe-S_{eq} bond distances are 2.338 and 2.348 Å, respectively, The sum of all five (Fe-N (×3) plus Fe-S (×2)) bond distances are 11.136 and 12.206 Å, indicating that the former molecule is more crowded than the latter.

There are two derivatives, $[Fe^{II}(H_2O)_6][Fe^{II}(\eta^4\text{-}C_6H_5O_7)(H_2O)_2]\bullet 2H_2O$ [16] and $[Fe^{II}(dmf)_6](ClO_4)_2$ [17] which contain two crystalographically independent molecules. Each iron(II) atom is six – coordinated by the respective O donor atoms, (FeO_6) with different degree of distortion (Table 2).

Yellow trigonal $[Fe^{II}(MeCN)_6][Fe^{III}Cl_4]_2$ [18] contains two crystallographically independent $[Fe^{II}(MeCN)_6]^{2+}$ cations in which each iron(II) atom is hexacoordinated by six unidentate MeCN ligands (FeN_6). The inner coordination sphere around Fe(II) atoms differ in mean Fe-N bond distances of 2.176(11,65) and 2.163(3,0) Å the first number in parenthesis is e.s.d., and the second is maximum deviation from the mean. While in the latter molecule the iron(II) atom is symmetrically coordinated with the cis-N-Fe-N bond angles deviate from 90.0° only by 0.3 , and trans-N-Fe-N angles are 180°, in the former the angles deviate by 5.0° and 6.5°, respectively. This

Table 2. Crystallographic and structural data for monomeric iron coordination compounds – crystallographic independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Fe – L [Å]	L – Fe – L [°]	Ref.
$Fe^0(Bu^tNC)_5$ (yellow)	m $P2_1/n$ 8	18.930(3) 11.529(3) 28.968(8)	108.63(1)	FeC_5	C_{eq}[b] 1.817(10,18) C_{ax} 1.824(7,13)	C_{eq},C_{eq}[b] 119.9(4,25.3) C_{eq},C_{ax} 91.0(4,10.4) C_{ax},C_{ax} 164.5(4)	9
				FeC_5	C_{eq}[b] 1.825(9,15) C_{ax} 1.835(8,1)	C_{eq},C_{eq}[b] 119.9(4,16.4) C_{eq},C_{ax} 90.5(4,10.5) C_{ax},C_{ax} 167.2(4)	
$(sacsac)_2[Fe^{II}Cl_4]$ (deep red)	m C2/c 4	17.68(1) 7.65(1) 15.60(1)	122.0(1)	$FeCl_4$ $FeCl_4$	Cl 2.313(1,23) Cl 2.315(2,22)	Cl,Cl 109.5(6,6.3) Cl,Cl 109.5(2,6.6)	10
$Fe^{II}Cl_2(\eta^2$-dippe) (lavender)	or Pbca 16	24.66(1) 22.67(1) 14.995(6)		$FeCl_2P_2$	Cl 2.23(1,0) P 2.47(1,0)	Cl,Cl 118.0(4) P,P 83.7(3)[c] Cl,P 112.5(5,1.8)	11
				$FeCl_2P_2$	Cl 2.25(1,4) P 2.44(1,2)	Cl,Cl 116.2(4) P,P 84.0(3)[c] Cl,P 113.1(4,1.7)	
$[Fe^{II}(\eta^2$-opdp)$_2$i]•1.85CH_2Cl_2 (pale brown)	m $P2_1/a$ 4	22.567(5) 9.672(5) 26.843(5)	99.10	FeP_4I	P_{eq} 2.336(5,26) I_{ap} 2.632(5)	P,P 80.5(2,0)[c] P,I 94.7(2,1.5)	12
				FeP_4I	P_{eq} 2.351(5 ,28) I_{ap} 2.646(5)	P,P 80.2(2,0)[c] P,I 95.3(2,2.5)	
$[Fe^{II}(\eta^4$-time)Cl]Cl• 0.5MeOH•0.5H_2O (colourless)	tr P-1 4	11.823(8) 13.045(3) 13.922(2)	99.66(2) 94.41(3) 108.66(5)	FeN_4Cl	N_{eq} 2.105(4,9) Cl_{eq} 2.308(1) N_{ap} 2.184(4,31)	N_{eq},N_{eq} 116.9(1) N_{eq},Cl_{eq} 108.9(1,12.8) N_{ax},Cl_{eq} 109.0(1,15.1) N_{ax},N_{ax} 165.2(1)	13
				FeN_4Cl	N_{eq} 2.089(4,9) Cl_{eq} 2.307(1) N_{ap} 2.156(4,29)	N_{eq},N_{eq} 117.7(2) N_{eq},Cl_{eq} 105.8(1,9.6) N_{ax},Cl_{eq} 109.6(1,16.91) N_{ax},N_{ax} 168.8(1)	
$[Fe^{II}(\eta^4$-$p_4)Br]$ BPh_4•CH_2Cl_2 (green)	tr P-1 2	13.549(9) 19.058(12) 12.475(8)	72.0(1) 82.4(1) 81.2(1)	FeP_4Br	P_{eq} 2.198(6,17) Br_{eq} 2.361(4) P_{ax} 2.274(5,25)	P_{eq},P_{eq} 105.0(2) P_{eq},P_{ax} 86.4(2,10.8)[c] P_{ax},P_{ax} 164.1(2) P_{eq},Br_{eq} 127.4(2,3.1) P_{ax},Br_{eq} 96.2(2,5)	14
				FeP_4Br	P_{eq} 2.163(4,23) Br_{eq} 2.338(3) P_{ax} 2.241(4,6)	P_{eq},P_{eq} 100.5(2) P_{eq},P_{ax} 86.5(2,10.4)[c] P_{ax},P_{ax} 165.2(2) P_{eq},Br_{eq} 129.7(1,1.2) P_{ax},Br_{eq} 95.6(1,3)	
$[Fe^{II}(\eta^5$-tsalmah)] (deep red)	m $P2_1/n$ 8	21.016(9) 13.015(7) 15.476(8)	91.98(9)	FeN_3S_2	N_{eq} 2.20(1) S_{eq} 2.338(6,13) N_{ax} 2.13(2,2)	N_{eq},N_{eq} 88.5(6,4)[d] N_{eq},S_{eq} 115.3(4,2) N_{ax},S_{eq} 90.7(4,3.2)[d] S_{eq},S_{eq} 129.4(2) N_{ax},N_{ax} 176.1(6)	15
				FeN_3S_2	N_{eq} 2.23(2) S_{eq} 2.348(6,8) N_{ax} 2.14(2,2)	N_{eq},N_{eq} 86.5(6,0)[d] N_{eq},S_{eq} 117.1(5,3.2) N_{ax},S_{eq} 91.7(5,3.2)[d] S_{eq},S_{eq} 125.7(2) N_{ax},N_{ax} 172.4(6)	
$[Fe^{II}(H_2O)_6]\{Fe^{II}(\eta^4$-$C_6H_5O_7)(H_2O)_2]$•2 H_2O (not given)	m $P2_1/n$ 2	20.400(3) 6.710(1) 9.173(2)	96.99(1)	FeO_6	H_2O 2.123(3,9)	O,O 92.0(1,1.2)	16
				FeO_6	O_{eq} 2.131(2,97) H_2O_{eq} 2.090(2,0) O_{ax} 2.116(2,0)	O_{eq},O_{eq} 90.5(1,15.6) 166.3(1,2) O_{eq},O_{ax} 90.0(1,11.8) O_{ax},O_{ax} 174.6(1,0)	
$[Fe^{II}(dmf)_6](ClO_4)_2$ (not given) at 130 K	m $P2_1/b$ 4	14.634(8) 20.915(3) 10.790(5)	91.88(5)	FeO_6	dmf O 2.095(14,11)	O,O 90.0(5,3.7) 180	17
				FeO_6	dmf O 2.096(15,8)	O,O 90.0(6,2.3) 180	
$[Fe^{II}(MeCN)_6]$ $[Fe^{III}Cl_4]_2$ (yellow)	trg P-3 1	11.682(6) 6.134(4)		FeN_6	N 2.176(11,65)	N,N 90.0(4,5.0) 173.5(3)	18
				FeN_6	N 2.1693(,0)	N,N 90.0(1,3) 180	

Continued Table 2. Crystallographic and structural data for monomeric iron coordination compounds – crystallographic independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Fe – L [Å]	L – Fe – L [°]	Ref.
[Fe^{II}(η^4-tpp)(Pr^iNO)•(Pr^iNH_2)] (dark)	tr P-1 2	10.885(11) 15.247(19) 15.516(24)	114.67(10) 94.73(13) 89.25(19)	FeN_6 FeN_6	tpp,N_{eq} 1.993(7,12) Pr^iON_{ax} 1.862(14) $Pr^iH_2N_{ax}$ 2.105(5) tpp,N_{eq} 1.993(8,3) Pr^iON_{ax} 1.867(13,1) $Pr^iH_2N_{ax}$ 2.094(13)	N_{ax},N_{ax} 176.8(5) N_{ax},N_{ax} 178.4(6)	19
[Fe^{II}(η^3-bamp)$_2$]Cl_2•1.67H_2O (dark brown)	m I2/a 12	16.562(1) 9.704(1) 36.591(2)	 92.21(1) 	FeN_6 FeN_6	N 2.176(3,84) N 2.199(3,62)	N,N 78.58(10,64)[c] 98.25(10,9.70) 153.14(10,16) 175.94(10) N,N 75.45(10,15)[c] 98.68(10,12.93) 148.94(10) 170.84(10)	20
[Fe^{II}{η^3-HB(pz)$_3$}$_2$] (not given)	m $P2_1/c$ 4	12.258(9) 11.606(2) 16.518(3)	 107.56(2) 	FeN_6 FeN_6	N 1.975(3,5) N 1.970(3,10)	N,N 88.2(2,1)[d] N,N 88.3(2,3)[d]	21
[Fe^{II}(η^6-tpen)$(ClO_4)_2$•0.66H_2O (brownish red)	m C2/c 12	40.67(2) 9.497(4) 23.946(9)	 108.42(4) 	FeN_6 FeN_6	N 2.019(8,27) N 1.994(9,27)	N,N 87.0(3,14.7)[c] 88.9(3,9.8 112.4(3) 168.2(3,7.3 N,N 110.9(3) 173.2(3,6.5)	22
at 358 K	m C2/c 12	41.00(2) 9.517(5) 24.21(1)	 109.46(4) 	FeN_6 FeN_6	N 2.07(1,6) N 2.05(1,4)	N,N 87.0(5,16.5) 88.3(5,11.0) 112.4(3) 165.6(5,9.7) N,N 116.1(5) 169.9(5,7.7)	22
[Fe^{II}{η^2-S_2P(p-C_6H_4Me)$_2$}$_2$(tht)$_2$]tht (white yellow) at 140 K	tr P-1 1	9.204(3) 11.378(2) 11.389(4)	97.41(3) 114.00(3) 100.69(2)	FeS_6 FeS_6	^{2},S_{eq} 2.507(1,8) tht S_{ax} 2.650(2,0) ^{2},S_{eq} 2.507(1,8) tht S_{ax} 2.704(4,0)	S,S 82.2(1)[e] 90.4(14.7) 180 S,S 82.2(1,1)[c] 90.4(1,7.0) 180	23
[Fe^{II}(η^3-[9]aneS_3(η^3-[9]aneS_3(O)]ClO_4•2NaClO_4H_2O (orange – brown)	tr P-1 4	10.145(7) 12.323(6) 12.465(6)	82.91(4) 86.09(4) 83.16(5)	FeS_6 FeS_6	S_{eq} 2.255(1,5) O,S_{ax} 2.205(1,0) S_{eq} 2.261(1,3) O,S_{ax} 2.209(1,0)	S,S 89.9(1,1)[c] 180.0(1) S,S 89.8(1,1)[c] 180.0(1)	24
Cs[Fe^{II}(η^2-ens)$_3$]•H_2O (not given)	m $P2_1/c$ 2	14.97(1) 14.07(1) 14.05(1)	 94.31(4) 	FeO_3N_3 FeO_3N_3	O 1.926(12,17) N 1.857(13,4) O 1.918(11,8) N 1.874(11,10)	O,N 80.8(5,1)[c] O,N 80.9(5,0)[c]	25a
(NH_4)[Fe^{II}(η^2-vio)$_3$]•4.5H_2O (deep blue)	tr P-1 4	16.242(3) 15.690(3) 9.848(2)	90.95(2) 106.99(2) 74.20(2)	FeO_3N_3 FeO_3N_3	O 1.981(7,9) N 1.865(9,5) O 1.987(8,8) N 1.888(9,4)	O,O 90.3(3,1.3) N,N 94.9(4,1.0) O,N 84.0(3,4)[c] 91.2(4,2.7) 173.7(4,1.5) O,O 88.4(3,4.3) N,N 93.9(4,1.2) O,N 83.5(4,6)[c] 94.6(4,2.9) 171.2(4,4.0)	25b
($C_{22}H_{25}O_6$)[$Fe^{III}Cl_4$] (orange)	m $P2_1/a$ 4	17.04 9.69 15.66	 96.35 	$FeCl_4$ $FeCl_4$	Cl 2.09 2.19(x3) 2.14(-,3) 2.25	Cl,Cl 109.5(-,5.5) Cl,Cl 109.5(-,4.5)	26

Continued Table 2. Crystallographic and structural data for monomeric iron coordination compounds – crystallographic independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Fe – L [Å]	L – Fe – L [°]	Ref.
$[Fe^{III}(\eta^4\text{-tpp})(OSO_3H)]\bullet 0.5C_6H_6$ (deep purple)	m P2/c 8	16.981(5) 13.559(3) 33.456(5)	 99.88(8) 	FeN_4O FeN_4O	N_{eq} 2.045(5,12) O_{ap} 1.919(4) N_{eq} 2.040(4,11) O_{ap} 1.934(4)	N,N 87.7(2,1.2)[d] 157.27(19,67) N,O 101.3(2,1.6) N,N 87.55(18,59)[d] 156.14(19,42) N,O 101.9(2,2.2)	27
$[Fe^{III}(\eta^2\text{-}Pr^n{}_2NCS_2)_2I]$ (black)	tr C-1 8	27.644(6) 19.186(4) 8.694(2)	87.79(1) 88.72(1) 101.87(2)	FeS_4I FeS_4I	S_{eq} 2.281(4,19) I_{ap} 2.642(2) S_{eq} 2.283(5,10) I_{ap} 2.612(2)	S,S 76.3(2,1)[e] 96.7(2,1.2) 151.1(1,5.5) S,I 104.4(1,3.0) S,S 76.2(2,2)[e] 96.3(2,4) 150.5(2,3.8) S,I 104.8(2,3.7)	28
$[Fe^{III}(\eta^4\text{-}C_{20}H_{14}N_2O_2)Cl]$[f] (purple)	tr P-1 3	15.106(7) 13.570(5) 7.386(3)	101.55(2) 94.18(2) 92.49(2)	FeO_2N_2Cl FeO_2N_2Cl FeO_2N_2Cl 	O_{eq} 1.875(4,7) N_{eq} 2.104(5,5) Cl_{ap} 2.230(2) O_{eq} 1.900(4,5) N_{eq} 2.091(5,1) Cl_{ap} 2.232(2) O_{eq} 1.887(5,2) N_{eq} 2.102(5,14) Cl_{ap} 2.228(2)	O,O 92.0(2) N,N 76.6(2)[c] O,N 87.7(2,2)[d] 148.3(2,9) O,Cl 108.2(2,3) N,Cl 102.1(2,1.1) O,O 91.2(2) N,N 76.5(2) O,N 88.0(2,0) 151.6(2,0) O,Cl 110.0(2,0) N,Cl 102.4(2,0) O,O 90.6(2) N,N 76.8(2)[e] O,N 87.6(2,0)[d] 149.4(2,0) O,Cl 108.3(2,1.6) N,Cl 105.0(2,0)	29
$[Fe^{III}(pyOH)_6](NO_3)_3$[f] (dark red)	tr P-1 4	14.182(4) 14.493(3) 19.964(5)	73.12(2) 71.08(2) 89.26(2)	FeO_6 FeO_6 FeO_6	O 1.987(7,6) O 2.004(8,7) O 1.996(7,4)	O,O 89.9(3,2.6) 180.0 O,O 90.0(3,3.2) 180.0 O,O 90.0(3,3.6) 180.0	30
$[Fe^{III}(\eta^2\text{-dpm})_3]$ (red)	m C2/c 8	20.325(8) 17.350(7) 23.171(9)	 111.98(3) 	FeO_6 FeO_6	O 1.997(10,25) O 1.992(11,13)	O,O 84.8(5,2)[d] O,O 85.6(6,3)[d]	31
$[Fe^{III}(\eta^6\text{-}C_{31}H_{47}N_6O_{12}]$ (red) at 138 K	or $P2_12_12_1$ 8	8.683(13) 28.33(4) 36.84	 	FeO_6 FeO_6	O 1.99(2,3) 2.03(2,3) O 1.98(2,2) 2.02(2,3)	O,O 77.3(9,1.3)[c] 101.5(9,5.7) O,O 78.7(9,1.1)[c] 99.4(9,3.5)	32
$[Fe^{III}(\eta^6\text{-}C_{41}H_{64}N_9O_{17})]\bullet 10.5H_2O$ (red) at 138 K	tr P-1 2	13.578(2) 19.519(2) 11.018(3)	95.81(1) 91.63(1) 82.22(1)	FeO_6 FeO_6	O 2.002(12) 2.023(6) O 1.991(12) 2.039(6)	O,O 79.0(4)[c] O,O 77.9(3)[c]	33
$[Fe^{III}(\eta^6\text{-}C_{42}H_{57}N_{12}O_{16})]\bullet 13H_2O$ (red - brown) at 138(2) K	m I2 8	29.006(23) 14.511(13) 28.791(21)	 96.06(5) 	FeO_6 FeO_6	O 2.002(11,35) 2.012(11) O 2.003(11) 2.016(11,40)	O,O 79.9(4,2.1)[c] O,O 79.6(4,1.3)[c]	34
$(NMe_4)_3[Fe^{III}(NCS)_6]$ (red)	m C2/c 8	24.95(5) 9.30(3) 34.43(6	 125.22(6) 	FeN_6 FeN_6	N 2.05(2,1) N 2.05(2,2)	N,N 89.8(6,1.0) N,N 90.1(6,2.2) 178.8(6,4)	35

Continued Table 2. Crystallographic and structural data for monomeric iron coordination compounds – crystallographic independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Fe – L [Å]	L – Fe – L [°]	Ref.
[Fe^{III}{η^3-$HB(pz)_3$}$_2$]•[Fe^{III}{η^3-$HB(pz)_3$}Cl_3] (dark – red)	m $P2_1/n$ 4	12.063(1) 21.859(2) 14.121(2)	 97.77(1) 	FeN_6 FeN_6 FeN_3Cl_3	N 1.955(3,11) N 1.957(4,12) N 2.172(4,25) Cl 2.313(1,8)	N,N 88.7(1,2)[d] N,N 88.3(1,4)[d] N,N 81.7(1,2.1)[d] Cl,Cl 96.88(6,65) N,Cl 90.2(1,1.1) 169.2(1,7)	36
[Fe^{III}{η^3-$HB(pz)_3$}$_2$]NO_3 (dark – red)	tr P-1 2	11.252(2) 12.018(1) 12.189(2)	118.65(1) 96.34(1) 113.94(1)	FeN_6 FeN_6	N 1.956(5,4) N 1.952(5,8)	N,N 89.0(2,5)[d] N,N 88.6(2,7	37
[Fe^{III} (η^3- [9]aneN_3)$_2$]Cl_3•$5H_2O$[f] (red)	trg P3 3	8.069 31.322(9)	 	FeN_6 FeN_6 FeN_6	N 2.01(2,1) N 1.99(2,1) N 2.00(2,1)	N,N 86.1(10,1)[d] 178.9(9) N,N 85(1,1)[d] 178.8(9) N,N 83(1,0)[d] 180(1)	38
[Fe^{III}(η^4- tpp)(Him)$_2$]Cl•$CHCl_3$•H_2O (red)	tr P-1 2	13.33(2) 17.688(3) 11.213(2)	107.99(1) 94.70(1) 69.68(1)	FeN_6 FeN_6	tpp N_{eq} 1.994(3,9) imN_{ax} 1.977(3,0) tppN_{eq} 1.993(3,3) imN_{ax} 1.964(3,0)	N_{eq},N_{eq} 89.85(19)[d] N_{eq},N_{ax} 89.77(12,42) N_{eq},N_{eq} 89.36(11)[d] N_{eq},N_{ax} 89.87(12,46)	39
[Fe^{III}(η^4-tpp)(cmu)$_2$]SbF_6•1.5tol (red) at 115 K	tr P-1 2	10.406(5) 11.752(4) 28.538(10)	103.34(5) 108.35(3) 106.18(3)	FeN_6 FeN_6	tppN_{eq} 1.997(7,1) cmuN_{ax} 1.967(7,0) tppN_{eq} 1.995(7,12) cmuN_{ax} 1.979(7,0)	N_{eq},N_{ax} 90.2(3,4) N_{eq},N_{ax} 90.2(3,7)	40
[Fe^{III}(η^4-tpp)(NCS)(py)] (red)	tr P-1 2	11.423(2) 17.297(6) 11.324(2)	99.98(2) 109.43(1) 72.43(2)	FeN_6 FeN_6	tppN_{eq} 2.057(-,17) SCN_{ax} 2.030 pyN_{ax} 2.328 tppN_{eq} 2.002(-,10) SCN_{ax} 1.970 pyN_{ax} 2.402	N_{eq},N_{eq} 91.7(2)[d] N_{eq},N_{ax} 89.5(2,9.5) N_{eq},N_{eq} 91.0(3)[d] N_{eq},N_{ax} 90.0(3,10.0)	41
at 96 K	tr P-1 2	11.244(3) 17.132(4) 11.167(3)	100.01(2) 108.84(1) 72.49(1)	FeN_6 FeN_6	tppN_{eq} 1.988(4,3) SCN_{ax} 1.887 pyN_{ax} 2.027 tppN_{eq} 2.029(-,6) SCN_{ax} 1.908 pyN_{ax} 2.216	N_{eq},N_{eq} 90.1(2)[d] N_{eq},N_{ax} 89.9(-,9) N_{eq},N_{eq} 95.0(3)[d] N_{eq},N_{ax} 90.0(-,1.6)	41
[Fe^{III}(η^4-tmp)(1-MeHim)$_2$]•ClO_4 (not given)	tr P-1 2	13.929(2) 14.430(2) 15.105(3)	94.02(1) 105.97(1) 96.24(1)	FeN_6 FeN_6	tmpN$_{eq}$ 1.988(20,14) imN_{ax} 1.975(3,0) tmpN$_{eq}$ 1.987(1,1) imN_{ax} 1.965(3,0)	not given not given	42
[Fe^{III}(η^4-oep)(3-Clpy)$_2$]•ClO_4 (not given)	m $P2_1/a$ 8	20.779(7) 19.886(5) 22.142(6)	 101.18(2) 	FeN_6 FeN_6	oepN_{eq}2.003(4,1) ClpyN$_{ax}$ 2.314(4,6) oepN_{eq}2.008(4,9) ClpyN$_{ax}$ 2.303(4,19)	N_{eq},N_{eq} 90.0(2,5)[d] 179.2(2,4) N_{eq},N_{ax} 90.0(2,1.7) N_{ax},N_{ax} 178.6(1) N_{eq},N_{eq} 90.0(2,3)[d] 179.7(1,1) N_{eq},N_{ax} 90.0(2,18) N_{ax},N_{ax} 177.5(1)	43
[Fe^{III}(η^3-$MeBuNCS_2$)$_3$] (not given)	hx $P3_1/c$ 4	14.970(5) 14.390(3)	 	FeS_6 FeS_6	S 2.407(3,10) S 2.355(2,6)	S,S 73.2(1)[e] 93.6(4,1.7) 158.8(1) S,S 74.6(1)[e] 93.8(1,6) 162.1(2)	44

Continued Table 2. Crystallographic and structural data for monomeric iron coordination compounds – crystallographic independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	L – Fe – L [°]	Ref.
$H[Fe^{III}(\eta^3\text{-dipic})_2]\cdot 2H_2O$ (green)	or Pnn2 4	8.860(8) 11.007(2) 16.316(4)		FeO_4N_2	O 2.019(9,18) N 2.05(1,1)	O,O 93.5(4,3.9) 151.8(5,4) O,N 75.9(3,2)[c] 104.1(3,2) N,N 180(-)	45
				FeO_4N_2	O 2.026(7,14) N 2.06(1,3)	O,O 93.6(3,7) 151.1(5,5) O,N 75.6(2,3)[c] 104.5(2,3) N,N 180(-)	
$[Fe^{III}(\eta^4\text{-tttt})(H_2O)_2](ClO_4)_3\cdot H_2O$ (orange red)	tr P-1 2	12.416(3) 12.706(3) 8.940(2)	92.59(2) 104.62(2) 89.70(2)	FeN_4O_2	$ttttN_{eq}$ 1.954(5,6) H_2O_{ax} 1.901(4,0)	N,N 80.5(2)[c] 99.5(2)[d] N,O 90.0(2,2.8)	46
				FeN_4O_2	$ttttN_{eq}$ 1.951(5,4) H_2O_{ax} 1.912(4,0)	N,N 80.9(2)[c] 99.1(2)[d] N,O 90.0(2,2.6)	
$[Fe^{III}(\eta^4\text{-tpp})(tmso)_2]ClO_4$ (purple)	tr P-1 2	14.003(5) 15.246(5) 12.108(3)	113.20(2) 89.24(2) 76.67(4)	FeN_4O_2	$tppN_{eq}$ 2.048(3,4) $tmsoO_{ax}$ 2.087(3,0)	N,N 91.1(1)[d] N,O 87.2(1,3)	47
				FeN_4O_2	$tppN_{eq}$ 2.043(3,0) $tmsoO_{ax}$ 2.069(3,0)	N,N 90.01(1)[d] N,O 89.9(1,2)	
$[Fe^{III}(\eta^4\text{-tpp})(oTeF_5)(thf)]$ (dark purple)	tr P-1 1	9.542(3) 11.069(2) 11.843(3)	102.64(2) 104.45(2) 114.44(2)	FeN_4O_2	$tppN_{eq}$ 2.053(5,39) F_5TeO_{ax} 1.967(4) $thfO_{ax}$ 1.913(6)	N,N 89.5(9,1.6)[d] 169.2(2,3) N,O 95.3(2,1.1)	48
				FeN_4O_2	$tppN_{eq}$ 2.056(8,29) F_5TeO_{ax} 1.952(4) $thfO_{ax}$ 1.917(6)	N,N 89.3 (3,1.5)[d] 167.2(3,3) N,O 96.4(3,1.7)	
$[Fe^{III}(\eta^3\text{-3-oet-salapa})_2]ClO_4\cdot C_6H_6$ (black) at 128 K	m $P2_1/c$ 4	16.54(1) 17.35(1) 13.46(1)	116.267(18)	FeN_4O_2	N 1.958(5,0) N 2.028(5,0) O 1.852(4,0)	N,N 85.0(2)[d] N,O 91.1(2,6)[d]	49
				FeN_4O_2	N 1.961(5,0) N 2.032(5,0) O 1.850(4,0)	N,N 88.1(2)[d] N,O 92.9(2,2.3)[d]	
$[Fe^{III}(\eta^3\text{-3-oet-salapa})_2]ClO_4\cdot PhCl$ (black) at 158 K	m $P2_1/a$ 4	13.604(12) 17.475(13) 15.379(12)	109.24	FeN_4O_2	N 2.040(5,0) N 1.968(6,0) O 1.860(6,0)	N,N 85.2[d] N,O 92.0(-,8)[d]	49
				FeN_4O_2	N 2.046(6,0) N 1.969(6,0) O 1.866(6,0)	N,N 85.1[d] N,O 91.1(-,1.6)[d]	
$[Fe^{III}(\eta^3\text{-3-oet-salapa})_2]ClO_4\cdot PhBr$ (dark) at 163 K	m $P2_1/a$ 4	13.666(4) 17.554(4) 15.537(4)	109.20(2)	FeN_4O_2	N 2.027(8,0) N 1.115(7,0) O 1.900(7,0)	N,N 83.8[d] N,O 90.8(-,1.6)[d]	49
				FeN_4O_2	N 1.974(7,0) N 2.060(7,0) O 1.882(7,0)	N,N 84.6[d] N,O 91.1(-,6)[d]	
$[Fe^{III}(\eta^3\text{-3-allyl-salbzen})_2]\cdot NO_3$ (blue – purple)	m $P2_1/c$ 4	11.887(4) 21.686(6) 21.436(11)	99.71(5)	FeN_4O_2	N 1.983(5,6) N 2.121(5,27) O 1.897(5,45)	N,N 80.2(2,7) 90.03(19)[c] 98.6(2,1.3) 176.70(21) N,O 89.7(2,2.5) 90.4(2,7)[d] 170.1(2,4) O,O 94.36(18)	50
				FeN_4O_2	N 1.937(4,13) N 2.047(4,16) O 1.884(4,20)	N,N 82.7(2,2.0) 90.16(17)[c] 97.3(2,9) 179.03(20) N,O 87.2(2,1.0) 93.5(2,1.1)[d] 175.4(2,1.1) O,O 94.44(16)	

Continued Table 2. Crystallographic and structural data for monomeric iron coordination compounds – crystallographic independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	L – Fe – L [°]	Ref.
$[Fe^{III}(\eta^6$-tppim)]•$2H_2O$ (green)	tr P-1 2	12.785(3) 15.963(4) 12.104(3)	91.77(2) 105.46(2) 78.71(2)	FeN_4O_2 FeN_4O_2	N_{eq} 2.170(8,92) O_{ax} 2.002(5,0) N_{eq} 2.155(6,69) O_{ax} 1.995(7,0)	N,N 88.7(2,0)[d] O,N 86.6(2,2.5) N,N 89.6(3)[d] O,N 85.9(3,1.3)	51
$[Fe^{III}(\eta^4$-tpp)$(tht)_2]$ tht (purple)	tr P-1 2	13.225(3) 17.967(5) 10.283(2)	91.07(2) 99.22(2) 76.59(2)	FeN_4S_2 FeN_4S_2	tpp,N_{eq} 1.998(3,6) tht,S_{ax} 2.338(1,0) tpp,N_{eq} 1.995(3,5) tht,S_{ax} 2.334(1,0)	N,N 89.7(1,0)[d] N,S 87.7(1,1.0) N,N 89.8(1,0)[d] N,S 89.0(1,1.7)	52
$[Fe^{III}(\eta^4$-tim)$(SCH_2Ph)_2]PF_6$ (dark brown)	tr P-1 2	12.385(3) 12.483(2) 12.155(2)	97.446(12) 111.408(12) 63.960(13)	FeN_4S_2 FeN_4S_2	timN$_{eq}$ 1.929(4,13) S_{ax} 2.285(1,0) timN$_{eq}$ 1.926(4,5) S_{ax} 2.290(1,0)	N,N 80.1(2)[c] 99.9(2)[d] N.N 80.1(2)[c] 99.9(2)[d]	53
[Na(18-crown-6)] $[Fe^{III}(\eta^4$-tpp)$(SC_6HF_4)_2]$•C_6H_6 (not given)	tr P-1 2	12.628(4) 21.594(8) 12.881(4)	104.02(2) 98.26(2) 76.40(2)	FeN_4S_2 FeN_4S_2	tppN$_{eq}$ 1.999(3,6) S_{ax} 2.309(1,0) tppN$_{eq}$ 1.998(3,2) S_{ax} 2.316(1,0)	N,N 90.0(1,7)[d] N,S 90.0(1,5.5) N,N 90.0(1,6)[d] N,S 90.0(1,7.6)	54
$[Fe^{III}(\eta^2$-dppe$)_2(H)_2]$ (orange)	m $P2_1/c$ 8	18.565(5) 23.228(8) 24.067(7)	 107.20(2) 	FeP_4H_2 FeP_4H_2	P_{eq} 2.172(4,19) H_{ax} not given P_{eq} 2.168(4,13) H_{ax} not given	P,P 88.2(4,3)[c] 105.3(4,4.0) 155.8(4) P,P 88.5(4,3)[c] 106.8(4,1) 154.4(4)	55
fac-$[Fe^{III}(OPh_3)_3(NCS)_3]$ (red brown) at 80 K	trg R3 12	38.40(1) 12.092(9)	 	FeO_3N_3 FeO_3N_3	O 2.030(3,0) SCN 2.027(3,0) O 2.022(3,8) SCN 2.020(3,12)	O,O 87.3(2) O,N 91.6(2,2.5) 176.1(2) N,N 89.5(2) O,O 87.9(2,5) O,N 91.3(2,4.3) 175.8(2,1.3) N,N 89.6(2,3)	56
K$[Fe^{III}(\eta^4$-acacen$)(CN)_2]$•$2H_2O$ (deep green)	trg $P3_1$ 6	11.873(3) 15.002(145)	 120.0	$FeO_2N_2C_2$ $FeO_2N_2C_2$	O_{eq} 1.919(7,4) N_{eq} 1.919(8,3) NC_{ax} 1.998(12,14) O_{eq} 1.936(6,2) N_{eq} 1.919(7,1) NC_{ax} 1.997(10,8)	O,O 86.0(2) N,N 84.9(3)[c] O.N 94.6(3,5)[d] 178.9(3,9) O,C 89.7(4,2.4) N,C 90.4(4,2.3) C,C 178.9(4) O,O 83.2(2) N,N 85.4 (3)[c] O,N 95.7(3,2)[d] 178.0(3,0) O,C 89.4(3,1.5) N,C 90.6(3,2.3) C,C 177.9(4)	57
$(NH_4)[Fe^{III}(\eta^3$-3,5-$Cl_2tsa)_2]$•$1.5H_2O$ (dark)	m $P12_1/a1$ 4	20.273(7) 27.437(9) 8.852(5)	 98.80(8) 	$FeO_2N_2S_2$ $FeO_2N_2S_2$	O 1.929(8,24) N 1.955(9,6) S 2.262(3,12) O 1.967(9,12) N 2.064(10,2) S 2.401(4,20)	O,O 85.9(3) N,N 176.3(4) S,S 89.4(1) O,N 89.8(3,9) 92.9(4,5)[d] O,S 92.4(3,9) 176.7(3,1.6) N,S 84.3(3,9)[c] 93.2(3,5) O,O 88.4(3) N,N 173.9(4) S,S 90.7(1) O,N 87.8(3,7) 96.2(4,1.2)[d] O,S 91.9(3,9) 167.1(3,7) N,S 79.4(2,1)[c] 96.7(3,1.9)	58

Continued Table 2. Crystallographic and structural data for monomeric iron coordination compounds – crystallographic independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	L – Fe – L [°]	Ref.
at 103 K	m $P12_1/a1$ 4	20.203(7) 27.117(9) 8.705(4)	99.05(9)	$FeO_2N_2S_2$	O 1.926(11,19) N 1.950(12,7) S 2.255(5,17)	O,O 85.9(4) N,N 175.3(5) S,S 89.4(2) O,N 90.3(5,4.3)[d] 90.5(5,1.6) O,S 92.4(3,1.0) 177.3(4,1.9) N,S 84.6(4,5)[c] 92.1(4,6)	58
				$FeO_2N_2S_2$	O 1.943(10,3) N 1.954(15,17) S 2.309(5,23)	O,O 86.0(4) N,N 176.4(5) S,S 88.7(2) O,N 90.5(5,2)[d] 92.0(5,8) O,S 93.1(3,1.1) 172.9(4,4) N,S 82.6(4,0)[c] 95.0(4,1.1)	
$K[Fe^{III}(\eta^3\text{-}3,5\text{-}Cl_2tsa)_2]\bullet 1.5H_2O$ (dark)	m $P2_1/a$ 4	20.221(8) 27.210(9) 8.916(5)	98.08(8)	$FeO_2N_2S_2$	O 1.937(12,5) N 1.995(14,16) S 2.344(6,26)	O,O 88.5(4) N,N 173.7(5) S,S 91.4(2) O,N 91.4(5,2.0)[d] 93.1(5,1.3) O,S 90.5(4,2.3) 172.2(4,2.3) N,S 81.2(4,1)[c] 94.5(5,1.0)	59
				$FeO_2N_2S_2$	O 1.944(11,2) N 2.049(15,6) S 2.416(5,12)	O,O 88.1(5) N,N 174.4(5) S,S 89.8(2) O,N 86.5(5,3)[d] 97.3(5,1.4) O,S 92.9(3,5) 165.7(4,5) N,S 79.2(4,2)[c] 97.9(4,1.8)	
at 103 K	m $P2_1/a$ 4	20.090(7) 26.996(10) 8.695(4)	98.37(9)	$FeO_2N_2S_2$	O 1.929(14,24) N 1.882(17,29) S 2.254(7,23)	O,O 86.6(6) N,N 176.1(8) S,S 90.3(2) O,N 89.4(7.2) 93.2(7,1.4)[d] O,S 91.6(7,3) 176.8(5,1.6) N,S 84.4(6,5)[c] 93.2(5,1.8)	60
				$FeO_2N_2S_2$	O 1.931(13,20) N 1.919(17,12) S 2.295(6,2)	O,O 87.1(5) N,N 178.3(6) S,S 88.0(2) O,N 90.5(6.2)[d] 90.2(6,2) O,S 92.8(4,4) 174.18(5,1) N,S 83.7(5,1)[c] 95.2(5,3)	

[a]When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e. s. d., and the second is maximum deviation from the mean
[b]The chemical identity of the coordinated atom or ligand is specified in these columns
[c]Five-membered metallocyclic ring
[d]Six-membered metallocyclic ring
[e]Four-membered metallocyclic ring
[f]There are three crystallographically independent molecules

Table 3. Summary of the sum of Fe-L (x n) (n = 4,5 or 6) bond distances in distortion isomers (monomeric)

Chromophore	A [Å][a]	Fe-L [Å][b] more crowded	less crowded
$Fe(0)C_5$	3.85	9.099	9.145
$Fe(II)Cl_4$	3.96	9.380	9.400
$Fe(II)Cl_2P_2$	4.10	11.976	12.050
$Fe(II)N_4Cl$	3.99	10.797	10.886
$Fe(II)N_3S_2$	4.29	11.136	11.206
$Fe(II)P_4Br$	5.38	11.146	11.305
$Fe(II)O_3N_2$	4.44	11.442	11.500
$Fe(II)P_4I$	5.57	12.016	12.050
$Fe(II)N_6$	4.50	12.350	12.431
$Fe(II)O_6$	4.38	12.622	12.657
$Fe(II)S_6$	7.02	14.379	14.449
$Fe(III)Cl_4$	3.96	8.66	8.67
$Fe(III)N_4O$	3.73	10.094	10.099
$Fe(III)O_4N_2Cl$	3.95	10.227	10.258
$Fe(III)N_4Cl$	3.99	10.388	10.491
$Fe(III)O_2N_2C_2$	4.50	11.672	11.704
$Fe(III)O_3N_3$	4.44	11.832	11.898
$Fe(III)N_4O_2$	4.46	11.950	12.037
$Fe(III)O_6$	4.38	11.994	12.032
$Fe(III)N_6$	4.50	11.996	12.077
$Fe(III)N_4S_2$	5.04	12.157	12.193
$Fe(III)O_4N_2$	4.42	12.176	12.224
$Fe(III)O_2N_2S_2$	5.00	12.252	12.864
$Fe(III)S_6$	7.02	14.295	14.589
$Fe(III)P_4H_2$	4.98	12.123[c]	13.334[c]

[a] *is the sum of the covalent radius of coordinated atoms*
[b] *is the sum of Fe-L bond distances*
[c] *is the sum of P(x4) bond distances, Fe-H(x2) are not available*

indicates that the former molecule deviates from O_h symmetry.

In dark triclinic $[Fe^{II}(\eta^4\text{-tpp})(Pr^iNO)(Pr^iNH_2)]$ [19] an unsymmetrical tetragonal – bipyramid (4 + 1 + 1) around each Fe(III) atom is created by tetradentate (N_4) tpp ligand (in plane) and Pr^iON and Pr^iNH_2 occupied an axial positions (Table 2). While the mean Fe-N_{eq} bond distances in the both molecules are equal (1.993 Å), the Fe-N_{ax} bond distances are 1.862 and 2.105 Å (molecule 1) and 1.863 and 2.094 Å, respectively. This indicates that the former molecule is somewhat more distorted than the latter.

In dark brown monoclinic $[Fe^{II}(\eta^3\text{-bamp})_2]Cl_2 \cdot 1.67H_2O$ [20] a pair of terdentate (N_3) bamp ligand form around each iron(II) atom a pseudo – octahedral coordination (FeN_6). The mean Fe-N bond distances are 2.176(3) Å (molecule 1) and 2.199(3) Å (molecule 2). The mean five – membered metallocyclic N-Fe-N bond angles are 78.6 and 75.5°, respectively. The inner coordination sphere around iron(II) atom in the former molecule is somewhat less thronged and less distorted than the latter molecule (Table 2).

In another monoclinic $[Fe^{II}\{\eta^3\text{-}HB(pz)_3\}_2]$ [21] a pair of terdentate (N_3) $HB(pz)_3$ ligand create around each iron(II) a pseudo – octahedral arrangement (FeN_6), with mean Fe-N bond distances and six – membered metallocyclic N-Fe-N bond angles of 1.975(3) Å and 88.2(2)° (molecule 1) and 1.970(3) Å and 88.2(2)° (molecule 2). The inner coordination sphere around iron(II) atoms in these molecules are less distorted than those in [20], as a mainly reason of six – against five – membered metallocyclic rings.

Structure of brown – red monoclinic derivative was studied at two different temperatures, room temperature and 358 K [22]. The structure consists of well separated $[Fe^{II}(\eta^6\text{-tpen})]^{2+}$ cation, ClO_4^- anions and water molecules (Fig. 2). The hexadentate (N_6) tpen ligand forms low – spin derivative with a FeN_6 core with mean Fe-N bond distances of 2.019 Å at room temperature (molecule 1) and 1.994 Å (molecule 2). The values are somewhat shorter than those found at 358 K, 2.07 *vs.* 2.05 Å, respectively.

In pale – yellow triclinic high – spin $[Fe^{II}\{\eta^2\text{-}S_2P(p\text{-}C_6H_4Me)_2\}_2(tht)_2$ [23] a pair of homo – bidentate (S_2) di(p-tolyl)dithiophosphinate (1-) anions created a plane with the mean Fe-S_{eq} bond distance of 2.507(1) Å in both molecules. A pair of tetrahydrothiophene ligands occupied axial positions with mean Fe-S_{ax} bond distances of 2.650(2,0) (molecule 1) and 2.704(4,0) Å (molecule 2). The value of the T parameter ($T = R_S/R_L$), indicating the degree of tetragonal distortion around the iron(II) centers, decreases in the order 0.946 (molecule 1) > 0.927 (molecule 2).

In orange – brown triclinic low – spin $\{Fe^{II}_2\{\eta^3\text{-}[9]\bullet aneS_3)(\eta^3\text{-}[9]aneS_3(O)](ClO_4)_2 \bullet 2NaClO_4 \bullet H_2O$ [24] two terdentate (S_3) ligands create a trigonal antiprism coordination around each iron(II) atom (FeS_6). The mean Fe-S ([9](aneS_3) and Fe-S ([9]aneS_3(O) bond distances (molecule 1 *vs.* molecule 2) are 2.255(1) and 2.205(1) Å *vs.* 2.261(1) and 2.209(1) Å. The sum of all six Fe-S bond distances is 13.38 and 13.41 Å, respectively.

There are two derivatives, monoclinic $Cs[Fe^{II}(\eta^2\text{-ens})_3] \bullet H_2O$ [25a] and triclinic $(NH_4[Fe^{II}(\eta^2\text{-vio})_3] \bullet 4.5H_2O$ [25b] in which three heterobidentate –O,N (ens or vio) create a rhombic symmetry around each iron(II) atom (FeO_3N_3) with different degree of distortion. Each derivative contains two crystallographically independent molecules. The mean Fe-O and Fe-N bond distances (molecule 1 *vs.* molecule 2) in [25a] are 1.925 and 1.857 Å *vs.* 1.918 and 1.874 Å and in [25b] the values are 1.981 and 1.865 Å *vs.* 1.987 and 1.888 Å. The mean values of the five – membered metallocyclic O-Fe-N bond angles are 80.8 and 80.9° in [25a] and 84.0 and 83.5° in [25b] (Table 2).

There are thirty seven iron(III) derivatives which contain two crystallographically independent molecules and another three iron(III) derivatives which contain three such molecules and their structural parameters are summarized in Table 2.

Orange monoclinic $(C_{22}H_{25}O_6)[FeCl_4]$ [26] is the only example in which iron(III) atom has a tetrahedral

arrangement ($FeCl_4$) with the mean Fe-Cl bond distance of 2.165 Å (molecule 1) and 2.168 Å (molecule 2). The maximum deviation of Cl-Fe-Cl bond angles from the ideal value of 109.5° is 5.5° (molecule 1) and 4.5° (molecule 2). This indicates that the inner coordination sphere around iron(III) atom in the former is somewhat more distorted than the latter.

In another three derivatives [27–29] each iron atom is five – coordinated (square pyramidal) with the chromophores FeN_4O [27], FeS_4I [28] and FeO_2N_2Cl [29]. In deep purple [Fe^{III}(η^4-tpp)(OSO_3H)]0.5 C_6H_6 [27] a tetradentate (N_4) type ligand form a plane with the mean Fe-N_{eq} bond distances (molecule 1 *vs.* molecule 2) of 2.046 *vs.* 2.040 Å. The apical position is occupied by O atom of OSO_3H group (Fe-O_{ap} = 1.919(4) and 1.934(4) Å). The displacement of the iron(III) atom from the plane (N_4) toward the apical oxygen atom is about 0.42 Å.

In black triclinic [Fe^{III}(η^2-Pr^i_2NCS)$_2$I] [28] a pair of homobidentate (S_2) $Pr^i_2NCS_2^-$ ligands created a plane and apical position is occupied by iodine atom (FeS_4I). The mean Fe-S_{eq} and Fe-I_{ap} bond distances (molecule 1 *vs.* molecule 2) are 2.281 and 2.642(2) Å *vs.* 2.283 and 2.612(2) Å. The displacement of the iron(III) atom from the basal plane (N_4) toward the apical iodine atom are 0.586 and 0.580 Å, respectively.

Purple triclinic [Fe^{III}(η^4-$C_{20}H_{14}N_2O_2$)Cl] [29] contains three crystallographic independent molecules. In each molecule hetero – tetradentate (O_2N_2) $C_{20}H_{14}N_2O_2^{2-}$ ligand form a basal plane and chloride atom occupied an apical position. The mean Fe-O_{eq}, Fe-N_{eq}, Fe-Cl_{ap} bond distance and displacement of the iron atom from the basal plane (N_4) (molecule 1 *vs.* molecule 2 *vs.* molecule 3) are: 1.875(4), 2.104(5), 2.230(2) and 0.52(1) Å *vs.* 1.900(4), 2.091(5), 2.232(2), and 0.52(1) Å *vs.* 1.887(5), 2.102(5), 2.228(2) and 0.53(1) Å. The values of the five – membered metallocyclic N-Fe-N bond angles and of six – membered metallocyclic O-Fe- N bond angles are: 76.6(2) and 87.2° (mean) (molecule 1), 76.5(2) and 88.0(2)° (mean) (molecule 2) and 76.8(2) and 87.6(2)° (mean) (molecule 3).

In the remaining iron(III) derivatives, each iron(III) atom is six-coordinated, with the chromophores: FeO_6[30–34], FeN_6 [30,35–43], FeS_6 [44], FeO_4N_2 [45], FeN_4O_2 [46–51], FeN_4S_2 [52–54], FeP_4H_2 [55], FeO_3N_3 [25,56], $FeO_2N_2C_2$ [57], and $FeO_2N_2S_2$ [58–60]. Dark red triclinic [Fe^{III}($pyOH$)$_6$](NO_3)$_2$ [30] contains three crystallographic independent molecules. Hexacoordination around each iron(III) atom is formed by six unidentate O donor atoms of pyOH ligand (FeO_6). The mean Fe-O bond distances are 1.987 Å (molecule 1) 2.004 Å (molecule 2) and 1.996 Å (molecule 3). The maximum deviation of cis-O-Fe-O bond angles from the ideal 90.0° is 2.6, 3.2 and

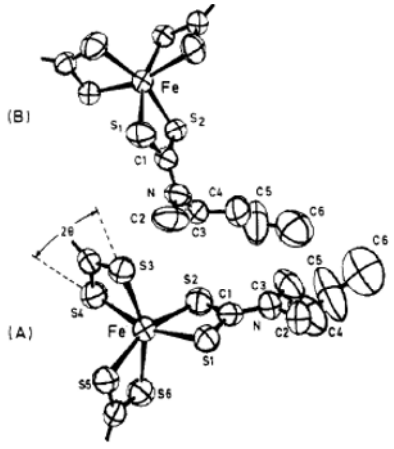

Figure 3. Structure of [Fe^{III}(η^2-$MeBuNCS_2$)$_3$] [44]

3.6°. This indicates that the degree of distortion increases in the order: molecule 1< molecule 2 < molecule 3.

In red [Fe^{III}(η^2-dpm)$_3$] [31] which contains two crystallographically independent molecules, three homo – bidentate (O_2) dpm(1-) ligands created a six – coordination around each iron(III) atom (FeO_6) with different degree of distortion. The mean Fe-O bond distances and the mean values of six – membered metallocyclic O-Fe-O bond angles (molecule 1 *vs.* molecule 2) are: 1.997 Å and 84.8° *vs.* 1.992 Å and 85.6°.

In another three red derivatives, orthorhombic [Fe^{III}(η^6-$C_{31}H_{47}N_6O_{12}$)] [32], triclinic [Fe^{III}(η^6-$C_{41}H_{64}N_9O_{17}$)]•10.5H_2O [33], and monoclinic [Fe^{III}(η^6-$C_{42}H_{57}N_{12}O_{16}$)]•13H_2O [34] which contain two crystallographically independent molecules a respective homo – hexadentate (O_6) ligands created an octahedral arrangement around each iron(III) atom with a different degree of distortion. The sum of Fe-O (x6) bond distances and the mean five – membered metallocyclic O-Fe-O bond angles (molecule 1 *vs.* molecule 2) are: 12.06 Å and 77.3° *vs.* 12.00 Å and 78.7° [32], 12.075 Å and 79.0° *vs.* 12.090 Å and 77.9° [33], 12.042 Å and 79.7° *vs.* 12.057 Å and 79.6° [34].

There are ten derivatives [35–43] in which each iron(III) atom is coordinated by six N donor atoms (FeN_6). Structure of red monoclinic derivative [35] consists of well; separated NH_4^+ cations and [Fe^{III}(NCS)$_6$]$^{3-}$ anions. In complex anion, six NCS^- groups form an octahedral arrangement with the mean Fe-N bond distances of 2.05 Å in both molecules. The cis- N-Fe-N bond angles deviated from the ideal 90.0° by 1.0° (molecule 1) and 2.2° (molecule 2). This indicates that the latter molecule is somewhat more distorted than the former.

There are two dark derivatives, monoclinic [Fe^{III}{η^3-HB(pz)$_3$}$_2$][Fe^{III}{η^3-HB(pz)$_3$}Cl_2] [36] and triclinic [Fe^{III}{η^3-

$HB(pz)_3\}_2]NO_3$ [37], which contain two crystallographic independent molecules. Structures of $[Fe^{III}\{\eta^3\text{-}HB(pz)_3\}_2]^+$ cations [36,37] are similar, in each a pair of terdentate $(N_3)HB(pz)_3$ ligands created a pseudo – octahedral coordination around each iron(III) atom (FeN_6). The mean Fe-N bond distances and six – membered metallocyclic N-Fe-N bond angles (molecule 1 *vs.* molecule 2) are 1.955 Å and 88.7° *vs.* 1.957 Å and 88.3° [36], 1.956 Å and 89° *vs.* 1.952 Å and 88.6° [37].

In red trigonal $Fe^{III}\{\eta^3\text{-}[9]aneN_3\}_2]Cl_3\bullet 5H_2O$ [38] two terdentate (N_3) [9]-ane N_3 ligands form around iron(III) atom a pseudo – octahedral arrangement (FeN_6). This derivative contains three crystallographically independent molecules with the mean Fe-N bond distances and six – membered metallocyclic N-Fe-N bond angles of: 2.01 Å and 86° (molecule 1), 1.99 Å and 85° (molecule 2), 2.00 Å and 83° (molecule 3).

In another five red derivatives, triclinic $[Fe^{III}(\eta^4\text{-}tpp)(Him)_2]\bullet Cl\bullet CHCl_3\bullet H_2O$ [39], triclinic$[Fe^{III}(\eta^4\text{-}tpp)(cmu)_2]SbF_6\bullet Cl\bullet 1.5$ [40], triclinic $[Fe^{III}(\eta^4\text{-}tpp)(NCS)(py)]$[41], triclinic $[Fe^{III}(\eta^4\text{-}tmp)(1\text{-}MeHim)_2](ClO_4)$ [42], and monoclinic $[Fe^{III}(\eta^4\text{-}oep)(3\text{-}Clpy)_2](ClO_4)$ [43] which contain two crystallographically independent molecules, a respective tetradentate (N_4) ligand form a basal plane and two unidentate (N) ligands occupied an axial position. In [39,40,42] each iron(III) atom has a contracted tetragonal bipyramidal environment with the mean Fe-N_{eq} and Fe-N_{ax} bond distances (molecule 1 *vs.* molecule 2) of 1.994 and 1.977 Å *vs.* 1.993 and 1.964 Å [39], 1.997 and 1.967 Å *vs.* 1.955 and 1.979 Å [40], 1.988 and 1.975 Å *vs.* 1.987 and 1.965 Å [42].

Structure of $[Fe^{III}(\eta^4\text{-}tpp)(NCS)(py)]$ [41] was studied at room temperature and at 96 K. The N donor atoms of the respective ligands created around each iron(III) an unsymmetrically elongated tetragonal bipyramid (4 + 1 + 1) with the mean Fe-N_{eq}, Fe-N_{ax}(NCS) and Fe-N_{ax}(py) bond distances (molecule 1 *vs.* molecule 2) of 2.057, 2.030 and 2.328 Å *vs.* 2.002, 1.970 and 2.402 Å at room temperature. At 96 K the Fe-N bond distances, with one exception, shortened with the values of 1.988, 1.883 and 2.027 Å *vs.* 2.029, 1.908 and 2.216 Å.

In $[Fe^{III}(\eta^4\text{-}oep)(3\text{-}Clpy)_2](ClO_4)$ [43] each iron (III) atom has an elongated tetragonal bipyramidal environment (4 + 2). The mean Fe-N_{eq} and Fe-N_{ax} bond distances are 2.003 and 2.314 Å (molecule 1) and 2.008 and 2.303 Å (molecule 2).

In hexagonal $[Fe^{III}\eta^2\text{-}MeBuNCS_2)_3]$ [44] (Fig. 3) three hemobidentate (S_2) $MeBuNCS_2$ ligands form a pseudo – octahedral arrangement around each iron(III) atom (FeS_6). The mean Fe-S bond distances and four- membered metallocyclic S – Fe – S bond angles (molecule 1 *vs.* molecule 2) are 2.407Å and 73.2° *vs.* 2.355 Å and 74.6°. In green $H[Fe^{III}(\eta^3\text{-}dipic)_2]\bullet 2H_2O$ [45] a pair of heteroterdentate (O_2N) dipic ligands form a pseudo-octahedral arrangement around each iron(III) atom (FeO_4N_2). The mean Fe-O and Fe-N bond distances are 2.019 and 2.05 Å (molecule 1) and 2.026 and 2.06 Å (molecule 2).

There are eight derivatives [46–51] in which four N donor atoms with two O donor atoms form a pseudo – octahedral arrangement around each iron(III) atom (FeN_4O_2). In three coloured orange red $[Fe^{III}(\eta^4\text{-}tttt)(H_2O)_2](ClO_4)_3\bullet H_2O$ [46], purple $[Fe^{III}(\eta^4\text{-}tpp)(dmso)_2]ClO_4$ [47] and dark purple $[Fe^{III}(\eta^4\text{-}tpp)(OTeF_5)(thf)]$ [48] a tetradentate (N_4) ligand build up a basal plane and two O donor ligands occupied an axial positions.

In [46] each iron(III) atom has a symmetrical contracted tetragonal bipyramidal environment with the mean Fe-N_{eq} and Fe-O_{ax} bond distances (molecule 1 *vs.* molecule 2) of 1.954 and 1.901 Å *vs.* 1.951 and 1.910 Å. In [47] a symmetrical elongated tetragonal bipyramid with the respective bond distances of 2.048 and 2.087 Å *vs.* 2.043 and 2.069 Å. In [48] a unsymmetrical contracted tetragonal bipyramid (4+1+1) with the Fe-N_{eq} (mean), Fe-O_{ax} ($OTeF_5$) and Fe-O_{ax} (thf) bond distances of 2.053, 1.967 and 1.913 Å *vs.* 2.056, 1.952 and 1.917 Å (Table 3).

In another three black derivatives, $[Fe^{III}(\eta^3\text{-}3\text{-}oet\text{-}salapa)_2]ClO_4\bullet C_6H_6$ [49], $[Fe^{III}(\eta^3\text{-}3\text{-}oet\text{-}salapa)_2]ClO_4\bullet PhCl$ [49] and $[Fe^{III}(\eta^3\text{-}oet\text{-}salapa)_2]ClO_4\bullet PhBr$ [49], which are isostructural, two hetero – terdentate (N_2O) ligand created a trigonal distortion of octahedral coordination around each Fe(III) atom (FeN_4O_2). The Fe-L bond distances of the three pairs (Fe-N(×4), Fe-N(×2) and Fe-O(×2) (molecule 1 *vs.* molecule 2) are: 2.028, 1.958 and 1.852 Å *vs.* 2.032, 1.961 and 1.850 Å (solvent C_6H_6); 2.040, 1.968 and 1.861 Å *vs.* 2.046, 1.969 and 1.866 Å (PhCl); 2.115, 2,027 and 1.900 Å *vs.* 2.060, 1.974 and 1.882 Å (PhBr).

Structure of blue purple $[Fe^{III}\eta^3\text{-}3\text{-}allyl\text{-}salbzen)_2]\bullet NO_3$ [50] is similar to the previously. Pair of hetero – terdentate (N_2O) ligand create a pseudo – octahedral environment around each iron(III) atom (FeN_4O_2). The mean Te-N, Fe-N and Fe-O bond distances (molecule 1 *vs.* molecule 2) are: 2.121, 1.983 and 1.897 Å *vs.* 2.047, 1.937 and 1.884 Å.

In green $[Fe^{II}(\eta^6\text{-}tppim)]\bullet 2H_2O$ [51] hetero – hexadentate (N_4O_2) ligand created a contracted tetragonal bipyramid around iron(II) atom with N donor atoms in basal plane and O donor atoms occupied an axial positions. The mean Fe-N_{eq} and Fe-O_{ax} bond distances (molecule 1 *vs.* molecule 2) are: 2.170, and 2.002 Å *vs.* 2.155 and 1.995 Å.

In another three triclinic derivatives $[Fe^{II}(\eta^4\text{-}tpp)(tht)_2]$ tht [52], $[Fe^{III}(\eta^4\text{-}tim)SCH_2Ph)_2]PF_6$ [53] and [Na(18-crown-6)]$\bullet[Fe^{III}(\eta^4\text{-}tpp)(SC_6HF_4)_2]C_6H_6$ [54], respective

tetradentate (N_4) ligands created a basal plane and two unidentate S donor ligands occupied an axial positions around each iron atom (FeN_4S_2). In elongated tetragonal bipyramid the mean Fe-N_{eq} and Fe-S_{ax} bond distances (molecule 1 *vs.* molecule 2) are: 1.998 and 2.338 Å *vs.* 1.995 and 2.334 Å [52], 1.929 and 2.285 Å *vs.* 1.926 and 2.290 Å [53], 1.999 and 2.309 Å *vs.* 1.998 and 2.316 Å [54].

In orange [$Fe^{II}(\eta^2$-dppe)$(H)_2$] [55] a pair of homo-bidentate (P_2) dppe ligands created a basal plane and two hydride atoms occupied an axial positions. The mean Fe-P_{eq} bond distances are: 2.172 Å (molecule 1) and 2.168 Å (molecule 2). The Fe-H_{ax} bond distances are absent in the original paper.

In red brown trigonal fac – [$Fe^{III}(OPPh_3)_3(NCS)_3$] [56] three unidentate $OPPh_3$ ligands with three unidentate NCS^- groups form a pseudo – octahedral arrangement around iron(III) atom (FeO_3N_3). The mean Fe-O and Fe-N bond distances are: 2.030 and 2.027 Å (molecule 1) and 2.022 and 2.020 Å (molecule 2).

In deep green trigonal K[$Fe^{III}(\eta^4$-acacen$)(CN)_2$]•$2H_2O$ [57] hetero – tetradentate (O_2N_2) acacen ligand forms a basal plane and two CN groups occupied an axial positions ($FeO_2N_2C_2$). In elongated tetragonal bipyramid around iron(III) atom the mean Fe-O_{eq}, Fe-N_{eq} and Fe-C_{ax} bond distances (molecule 1 *vs.* molecule 2) are: 1.919, 1.919 and 1.998 Å and 1.936, 1.917 and 1.997 Å.

There are two dark monoclinic (NH_4)[$Fe^{III}(\eta^3$-3,5-Cl_2tsa$)_2$]•$1.5H_2O$ and K[$Fe^{III}(\eta^3$-3,5-Cl_2tsa$)_2$]•$1.5H_2O$ [58,59,60] which are isostructural. The structures were studied at room temperature and at 103 K. A trigonal distorted octahedron around each iron(III) atom is build up by a pair of hetero – terdentate (ONS) ligand. The mean Fe-O, Fe-N and Fe-S bond distances are: 1.929 (1.926), 1.955 (1.950) and 2.262 (2.255) Å *vs.* 1.967 (1.943), 2.064 (1.954) and 2.401 (2.309) Å [58]; 1.937 (1.929), 1.995 (1.882) and 2.344 (2.254) Å *vs.* 1.944 (1.931), 2.049 (1.919) and 2.416 (2.295) Å [59,60]. As can be seen, the Fe-L bond distances shortened with decreasing temperature.

Inspection of the data in Tables 1 and 2 reveals that the distortion isomers exist in the following crystal classes monoclinic (×30), triclinic (×23), hexagonal (×4), orthorhombic (×3), tetragonal and hexagonal (each ×3). The derivatives are coloured iron(0) yellow, iron(II) dark red (×8), yellow (×3), green (×2), brown (×1), lavender (×1); iron(III) red black (×8), purple (×8), orange (×3), green (×3). However, there are some examples for which colour were not given.

The mean Fe(0)-C bond distance is 1.825 (range 1.817 – 1.835 Å).The mean Fe^{II} -L bond distances elongated in the sequences: 2.045 Å (NL) < 2.100 Å (OL) < 2.316 Å (Cl)< 2.639 Å (I) < 2.677 Å (SL) (for unidentate

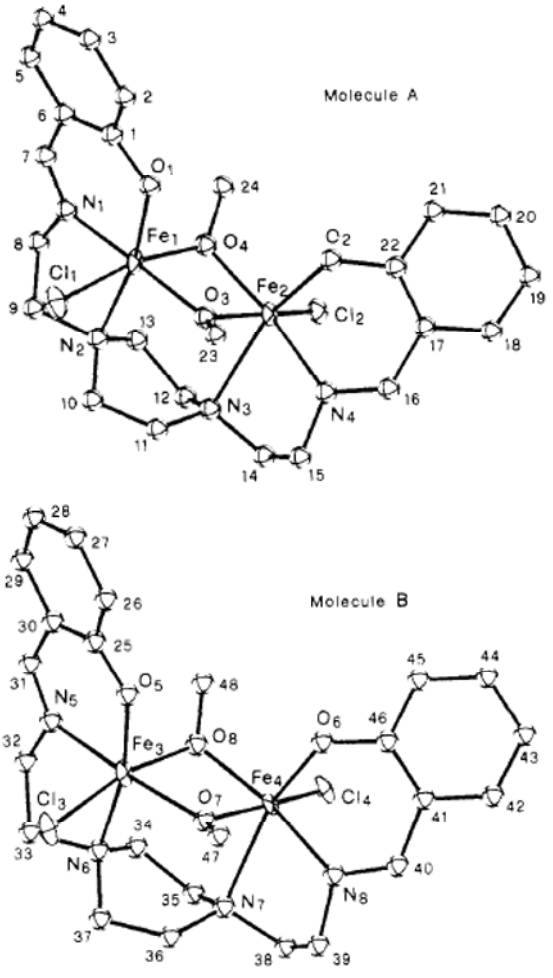

Figure 4. Structure of [$Fe^{III}_2(\mu$-OMe$)_2(\eta^6$-$C_{22}H_{26}N_4O_2)Cl_2$] [62]

ligands); 1.98 Å (hexa –NL) < 2.06 Å (tetra -NL) < 2.08 Å (ter –NL) < 2.125 Å (tetra –OL) < 2.400 Å (bi –PL) < 2.507 Å (bidentate SL). There are hetero – O + N donor ligands with the mean values Fe-O = 1.95 Å and Fe-N = 1.87 Å. Heteropenta – 3N + 2S, the mean values Fe-N = 2.175 Å and Fe-S = 2.345 Å. Correspondingly there is a wide variety of metallocyclic ring, and the effects of both steric and electronic factors play a role. Homo – as well as hetero – dentate ligands form metallocyclic rings with varying atoms and numbers of atoms in the ring. The mean value of the L-Fe(II)-L "bite" angles open in the order 77.0° (-NC_2N- unsaturation) < 81.6° (-NC_2N-, saturation) < 82.2° (-SCS-) < 82.4° (-OC_2N-) < 84.4°(-PC_2P-) < 86.2° (-NC_3N-) < 89.8° (-SC_2S-) < 91.2° (-NC_3S).

The mean Fe(III)-L bond distances, elongated in the sequences: 1.945 Å (OL) < 2.00 Å (CN) < 2.07 Å (NL) < 2.22 Å (Cl) < 2.31 Å (SL) (for unidentate ligands); 1.975 Å (ter – NL) < 1.995 Å (bi-OL) < 2.00 Å (tetra – NL) < 2.01 Å (hexa – OL) < 2.17 Å (bi-PL) < 2.38 Å

Table 4. Crystallographic and structural data for di- , tetra- and hexameric iron coordination compounds – independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	Fe – Fe [Å] Fe – L – Fe [Å] μL – Fe – μFe [°]	L –Fe – L [°]	Ref.
$[Fe^{III}_2(\mu\text{-}O)(\eta^4\text{-}acacen)_2]\bullet CH_2Cl_2$ (red brown)	tr P-1 4	11.923(3) 15.738(7) 18.554(8)	74.22(3) 76.25(2) 67.85(2)	FeO_3N_2	^{4}O[b] 1.962(8,7) μO 1.783(7,14) ^{4}N 2.077(9,29)	not given 154.6(4)	O,O[b] 87.6(3,2) μO,O 108.6(4,2.6) N,N 79.1(4,1.2)[c] O,N 87.0(4,8)[d] 145.7(4,5.6) μO,N 105.2(4,3.0)	61
				FeO_3N_2	^{4}O[b] 1.955(8,5) μO 1.780(7,5) ^{4}N 2.080(9,18)	not given 155.6(4)	O,O 88.5(3,8) μO,O 109.3(4,3.8) N,N 79.1(4,6)[c] O,N 86.5(4,6)[d] 145.4(4,5.8) μO,N 104.6(4,2.9)	
$[Fe^{III}_2(\mu\text{-}OMe)_2(\eta^6\text{-}C_{22}H_{26}N_4O_2)Cl_2]$ (brown)	m $P2_1/n$ 8	25.924(3) 18.923(3) 12.496(3)	90.12(2)	FeO_3N_2Cl	μMeO 1.99(2,2) ^{6}O 1.93(2,1) ^{6}N 2.28(3,19) Cl 2.31(1,1)	3.097(7) 103(1,1) 76.6(8,4)	μO,O 97.4(8,2.6) N,N 75.9(10,5)[c] O,N 88.1(10,5)[d] 163.6(9,2.0) μO,N 91.5(9,9.7) 169.4(10,2.2) O,Cl 96.2(6,9) μO,Cl 94.1(6,1.4) 165.6(6,2.1) N,Cl 90.4(7,3.7)	62
				FeO_3N_2Cl	μMeO 1.99(2,2) ^{6}O 1.91(2,1) ^{6}N 2.26(3,20) Cl 2.33(1,1)	3.115(7) 103(1,1) 76.6(8,7)	μO,O 97.7(8,2.9) N,N 76.7(10,1.3)[c] O,N 86.8(10,6)[d] 163.3(9,9) μO,N 90.7(9,9.1) 168.2(9,2.2) O,Cl 95.5(6,5) μO,Cl 94.7(6,1.2) 166.5(6,1.1) N,Cl 91.5(7,4.0)	
$(NEt_4)[Fe^{II,III}_2(\mu\text{-}salmp)_2]\bullet 2dmf$ (brown)	tr P-1 2	12.669(3) 12.992(2) 16.928(4)	99.27(2) 101.54(2) 95.91(2)	FeO_4N_2	O 1.982(9,12) μO 2.092(8,24) N 2.168(10,10)	3.116(4) 96.3(3) 83.7(3)	O,O 90.2(4) μO,O 94.1(4,5) N,N 159.8(4) μO,N 82.6(3,3.1)[c]	63
				FeO_4N_2	O 1.976(9,15) μO 2.090(9,12) N 2.179(10,2)	3.081(4) 94.9(4) 85.1(4)	O,O 90.4(4) μO,O 93.3(4,8) N,N 161.2(4) μO,N 83.2(3,2.4)[c]	
$[Fe^{III}(\mu\text{-}OCH_2CF_3)_2(\eta^2\text{-}acac)_4]$ (deep red)	m $P2_1/c$ 4	17.685(9) 10.055(7) 17.98(1)	90.52(7)	FeO_6	O 1.987(4,5) μO 2.018(3,1)	3.154(2) 102.8(2,0) 77.2(2)	O,O 87.6(2,1.2)[d] 95.3(2,0) 172.7(2,0) μO,O 87.9(2,4) 96.0(2,2.2) 169.1(2,2)	64
				FeO_6	O 1.994(3,7) μO 2.027(3,5)	3.159(2) 102.4(2,0) 77.6(2)	O,O 87.5(2,1.1)[d] 97.2(2,0) 172.4(2,0) μO,O 87.1(2,6) 96.0(2,4.8) 167.6(2,1.3)	
$[Fe^{III}_2(\mu\text{-}OH)_2\{\eta^3\text{-}HB(3,5\text{-}Pr^i_2pz)_3\}_2](C_5H_{12})_2$ (colourless) at 223 K	tr P-1 2	14.576(5) 22.508(4) 14.140(5)	93.18(3) 126.28(2) 97.99(3)	FeN_3O_2	N 2.17(2,7) μHO 2.03(1,1)	3.179(5) 103.3(5) 76.7(5)	not given	65
$(PPh_4)_2[Fe^{III}_2(\mu\text{-}S)_2(p\text{-}mph)_4]$ (orange red)	m $P2_1/a$ 4	16.308(5) 16.674(6) 24.456(9)	91.13(3)	FeO_2S_2	O 1.864(12,9) μS 2.221(5,2)	2.725(5) 75.7(2) 104.3(3)	O,O 97.2(6) O,μS 114.0(4,4.9)	66
				FeO_2S_2	O 1.877(11,3) μS 2.226(5,4)	2.722(5) 77.0(2) 103.03(3)	O,O 93.1(2) O,μS 115.4(4,3.1)	

Continued Table 4. Crystallographic and structural data for di- , tetra- and hexameric iron coordination compounds – independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	Fe – Fe [Å] Fe – L – Fe [Å] μL – Fe – μFe [°]	L –Fe – L [°]	Ref.
$[Fe_2^{II}(\mu\text{-}PBu^t_2)_2(Me_3P)_2Cl_2]$ (red brown)	m $P2_1/c$ 4	15.753(8) 15.875(8) 13.544(6)	94.69(2)	FeP_3Cl	P 2.449(5,0) μP 2.347(5,0) Cl 2.276(5,0)	2.805(3) 73.2(2) 106.8(2)	μP,P 115.8(2) P,Cl 89.0(2) μP,Cl 113.1(2)	67
				FeP_3Cl	P 2.478(5,0) μP 2.363(5,0) Cl 2.281(5,0)	2.840(3) 73.7(2) 106.3(2)	μP,P 118.5(2) P,Cl 88.8(2) μP,Cl 113.0(2)	
$[Fe_2^{0}(\mu\text{-}PPh_2)_2(NO)_4]$ (brown)	tr P-1 2	8.825(4) 17.440(5) 8.587(4)	93.81(4) 106.36(4) 87.64(4)	FeN_2P_2	N 1.650(5,1) μP 2.229(2,2)	2.687(1) 74.16(5) 105.84(6)	N,N 124.5(3) μP,N 103.6(2,3.5)	68
				FeN_2P_2	N 1.651(4,1) μP 2.231(2,2)	2.710(2) 74.83(5) 105.17(5)	N,N 122.5(4) μP,N 107.0(2,1.6)	
$[Fe_2^{+1}(\mu\text{-}SMe)_2(NO)_4]$ (not given)	tr P-1 2	7.059(1) 8.753(4) 9.514(3)	89.22(4) 68.69(3) 89.32(3)	FeN_2S_2	ON 1.664(4,2) μS 2.251(3,2)	2.686(4) not given	not given	69
				FeN_2S_2	ON 1.668(4,5) μS 2.256(3,2)	2.700(4) not given	not given	
$(NMeEt_3)_3[Fe_4^{II,III}(\mu_3\text{-}S)_4\bullet(SPh)_4]$ (black)	m Cc 8	11.426(5) 24.806(7) 39.147(10)	90.75(2)	FeS_4 (x4)	μ_3S 2.309(6,46) PhS 2.295(7,4)	2.743(4,29) 72.89(18,91)	μ_3S,μ_3S 104.8(2,1.7) μ_3S,S113.6(4,15.3)	70
				FeS_4 (x4)	μ_3S 2.309(6,45) PhS2.294(7,13)	2.744(4,29) 72.90(18,65)	μ_3S,μ_3S 104.8(2,1.3) μ_3S,S113.7(2,15.5)	
$(PPh_4)_2[Fe_4^{II,III}(\mu_3\text{-}Se)_4(\eta^3\text{-}dmtb)Cl]2dmf$[e] (black)	trg P3 3	24.733(3) 14.595(3)		$FeSe_3Cl$ (x1)	μ_3Se 2.413(3,0) Cl 2.243(3)	2.805(3,13) 71.2(1,5)	μ_3Se,μ_3Se 106.22 μ_3Se,Cl 112.56(7)	71
				$FeSe_3S$ (x3)	μ_3Se 2.407(3,7) Cl 2.261(4,0)		μ_3Se,μ_3Se 105.91(8,67) μ_3Se,S117.9(1,2.0)	
				$FeSe_3Cl$ (x1)	μ_3Se 2.412(3,0) Cl 2.194(7)	2.801(3,25) 71.0(1,8)	μ_3Se,μ_3Se 105.50 μ_3Se,Cl 113.20(7)	
				$FeSe_3S$ (x3)	μ_3Se 2.413(3,2) S 2.252(4,0)		μ_3Se,μ_3Se 106.38(8,1.0) μ_3Se,S115.8(1,1.2)	
				$FeSe_3Cl$ (x1)	μ_3Se 2.415(3) Cl 2.209(6)	2.814(3,13) 71.3(1,4)	μ_3Se,μ_3Se 106.29 μ_3Se,Cl115.8(1,1.2)	
				$FeSe_3S$ (x3)	μ_3Se 2.414(3,2) S 2.262(4,0)		μ_3Se,μ_3Se 105.80(9,53) μ_3Se,S117.5(1,2.0)	
$(NEt_4)_2[Fe_4^{II}(\mu\text{-}SCH_2Ph)_6Br_4]$ (dark brown)	tr P-1 4	12.874(2) 13.949(3) 43.272(8)	94.85(2) 94.07(2) 114.98(1)	FeS_3Br (x4)	μS 2.340(6,29) Br 2.404(3,15)	3.820(3,54) 109.5(2,2.2)	μS,μS108.6(2,16.5) μS,Br 110.1(2,7.5)	72
				FeS_3Br (x4)	μS 2.342(5,13) Br 2.413(3,13)	3.810(4,118) 108.5(2,4.6)	μS,μS 108.72(2,13.6) μS,Br 110.1(2,5.2)	
$[Fe_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}piv)_{12}]$ (yellow – brown)	tr P-1 2	13.818(3) 15.183(2) 23.063(4)	78.34(1) 80.54(2) 65.28(1)	FeO_5 (x2)	μ_3O 1.846(5) μ piv O 1.979(9,50)	3.148(2,22) 3.520(2,71) μ_3O 112.4(3,1.1) 135.2(3) μHO 122.2(3)	μO,O 94.4(2,2) 118.3(3,1.8) O,O 87.9(3,1.9) 123.5(3) 171.2(3) μ_3O,μHO94.5(2,1.2)	73
				FeO_6 (x4)	μ_3O 1.943(6,1) μ piv O 2.023(9,58) μHO 1.970(6,8)		μ_3O,O 91.9(3,1.9) 175.8(3,5) μHO,O 91.7(3,2.7) 171.5(3,1.4)	

Continued Table 4. Crystallographic and s tructural data for di- , tetra- and hexameric iron coordination compounds – independent molecules, distortion isomers[a]

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	Fe – Fe [Å] Fe – L – Fe [Å] μL – Fe – μFe [°]	L –Fe – L [°]	Ref.
$[Fe_6(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}piv)_{12}]$ (yellow – brown) (continued)				FeO_5 (x2)	μ_3O 1.843(5) μpivO 1.980(9,37)	3.151(2,5) 3.522(2,83) μ_3O 112.4(3,4) 135.2(3) μHO 122.2(3)	O,O 86.5(3,3.8) 172.5(3,7) μ_3O,O 95.2(2,6) 117.7(3,1.3) O,O 87.6(3,1.8) 124.7(3) 169.6(3)	73
				FeO_6 (x4)	μ_3O 1.949(7,3) μpivO 2.019(9,40) μHO 1.955(6,2)		μ_3O,μHO 95.1(3,1.1) μ_3O,O 91.7(2,6) 175.6(3,1.1) μHO,O 92.2(3,3.2) 171.3(4,5) O,O 86.4(3,4.3) 172.4(4,9)	

[a] *When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e. s. d., and the second is maximum deviation from the mean*
[b] *The chemical identity of the coordinated atom or ligand is specified in these columns*
[c] *Five-membered metallocyclic ring*
[d] *Six-membered metallocyclic ring*
[e] *There are three crystallographically independent molecules*

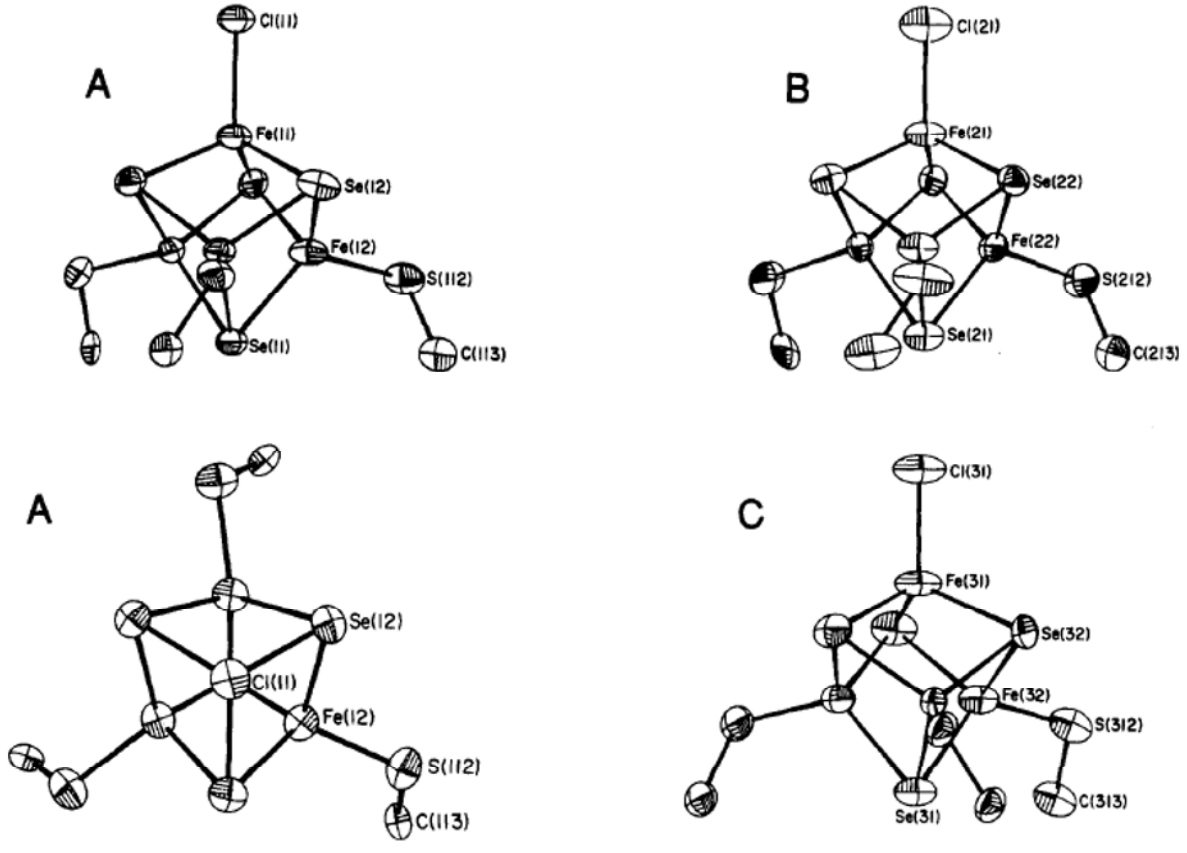

Figure 5. Structure of $[Fe^{II/III}(\mu_3\text{-}Se)_4(\eta^3\text{-}dmtb)Cl]^{2-}$ [71]

Table 5. Summary of the mean Fe-Fe distances and the sum of Fe-L(xn) (n = 4, 5 or 6) bond distances

Compound	Fe-Fe [Å]	Fe-L(xn) [Å] more crowded	Fe-Fe [Å]	Fe-L(xn) [Å] less crowded	Ref.
Dimeric					
FeN_2P_2	2.687(1)	7.758	2.710(2)	7.764	68
FeN_2S_2	2.686(4)	7.830	2.700(4)	7.848	69
FeO_2S_2	2.725(5)	8.170	2.722(5)	8.206	66
FeP_2Cl	2.805(3)	9.419	2.840(3)	9.485	67
FeO_3N_2		9.850		10.061	61
FeN_3O_2[a]	3.179(5)	10.570			65
FeO_6	3.154(2)	11.984	3.159(2)	12.030	64
FeO_4N_2	3.116(4)	12.484	3.081(4)	12.490	63
FeO_3N_2Cl	3.115(2)	12.740	3.097(2)	12.780	62
Tetrameric					
FeS_4(x4)	2.744(2)	9.221	2.743(2)	9.222	70
$FeSe_3Cl$(x1)[b]		9.482		9.504	71
$FeSe_3S$(x3)[b]					
FeS_3Br(x4)	3.820(3)	9.424	3.810(4)	9.439	72
Hexameric					
FeO_5(x2)	3.148(2)	9.762	3.151(2)	9.763	73
FeO_6(x4)	3.522(2)	11.990	3.520(2)	12.005	

[a]*only the mean values were published in the original paper*
[b]*there are three independent molecules*

(bi-SL) < 2.43 Å (terdentate SL). There is a wide variety of heteroligands: O plus N, 2O plus N, O plus 2N; O plus N plus S; 2O plus 2N, and 2O plus 4N , donor sites. Correspondingly there is a wide variety of metallocyclic rings (L-Fe(III) – L), which are open in the order: 74.6° (-SCS-) < 78.7° (OC_2O-) < 78.7° (NC_2N-, unsaturation) < 79.8° (OC_2N-) < 82.4° (-NC_2S-) < 85.2° (-OC_3O-) < 86.2° (-NC_2N-, saturation) < 88.4° (-PC_2P-) < 90.0° (-NC_3N-) < 91.0° (-OC_3N-).

The mean values of the sum of four-, five- and six Fe-L bond distances in the distortion isomeric derivatives (Tables 1 and 2), less or more crowded are summarized in Table 3. As can be seen there is a wide variety of the chromophores, four – coordinated iron atoms, Fe(II)Cl_4, Fe(II)Cl_2P_2, and Fe(III)Cl_4 are tetrahedral, five – Fe(O)C_5, Fe(II)N_3S_2 and Fe(II)P_4Br are trigonal bipyramid; all remainders, Fe(II)N_4Cl, Fe(II)P_4I, Fe(III)N_4O, Fe(III)N_4Cl and Fe(III)O_2N_2Cl are square – pyramidal; and six – coordinated are elongated tetragonal bipyramid, contracted tetragonal bipyramid, trigonal antiprism, and rhombic distorted (Tables 1 and 2). The deviation between the mean values more or less crowded, inner coordination sphere about iron atoms increases in the given orders; Fe(II): 0.048 Å (10.677 *vs.* 10.725 Å) four -< 0.062 Å (13.117 *vs.* 13.179 Å) six - < 0.082 Å (11.307 *vs.* 11.384 Å) five – coordinated; Fe(III); 0.01 Å (8.66 *vs.* 8.67 Å) four - < 0.047 Å (10.236 *vs.* 10.283 Å) five - < 0.144 Å (12.258 *vs.* 12.402 Å) six – coordinated. In the series of five – coordinated derivatives, the deviation between the mean values more *vs.* less crowded as well as their mean values increases with a lowering of the oxidation state of iron atom in the order: Fe(III) 0.047 Å (10.236 *vs.* 10.283 Å) < Fe(II) 0.082 Å (11.307 *vs.* 11.389 Å) < Fe(0) 0.146 Å (9.099 *vs.* 9.145 Å).

2.2. Di-, tetra-, hexameric complexes

There are thirteen derivatives (dimeric (×9), tetrameric (×3), and hexameric (×11) and twelve of them contain two crystallopraphic independent molecules and one derivative contains three such molecules. Crystallographic and structural parameters are presented in Table 4. As was mentioned there are nine dimeric derivatives [61–69], all of which contain two crystallographically independent molecules.

In red brown triclinic [Fe_2^{III}(μ-O)(η⁴-acacen)$_2$]CH_2Cl_2 [61] a square pyramidal arrangements around each iron(III) atom is built up by macrocyclic tetradentate acacen ligands (O_2N_2) which form a plane with μ-oxo in the apical position (FeO_3N_2). The Fe-O-Fe bridge angles are 154.6(4)° (molecule 1) and 155.6(4)° (molecule 2). The sum of all five (Fe-O(×3) plus Fe-N(x2)) bond distances are 10.06 and 9.85 Å, respectively. This indicates that the inner coordination sphere around iron(II) atom in the former molecule is somewhat less thronged that in the latter molecule.

In crystal structure of brown [Fe_2^{III} (μ-OMe)$_2$(η⁶-$C_{22}H_{26}N_4O_2$)•Cl_2] [62] (Fig. 4) is built up by discrete dimeric molecules. The asymmetric unit is formed by two crystallographically independent molecules. In each dimeric unit the Fe(III) atoms are symmetrically bridged by two methoxy groups. Each iron(III) atom is pseudo – octahedrally coordinated. (FeO_3N_2Cl). One oxygen and two nitrogen (cis) of hexadentate $C_{22}H_{26}N_4O_2$ (2-) occupy three coordination sites, the remaining three are occupied by the two bridging methoxy groups and a terminal chlorine atom. The Fe . . . Fe separations of 3.097(7) Å (molecule 1) and 3.115(7) Å (molecule 2) rule out a direct bond. The sum of (Fe-O(x3)

Table 6. Crystallographic and structural data for monomeric iron coordination compounds – cis – trans – isomers[a]

Compound (colour)	Cryst. cl. Cryst. gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Fe – L [Å]	L –Fe – L [°]	Ref.
$[Fe^{II}(\eta^2\text{-}\alpha\text{-pia})_3]I_2$ (dark red)	tr P-1 4	11.649(3) 16.933(6) 16.271(5)	116.86(2) 92.92(2) 120.02(2)	FeN_6 (cis) FeN_6 (trans)	N[b]2.063(6,3.0) N 2.200(7,11)	N,N[b] 79.9(2,2)[c] 93.5(3,2.8) 171.2(3,2.6) N,N 75.8(2,3)[c] 95.5(3,6.8) 163.0(2,4.4)	74
$[Fe^{II}(\eta^2\text{-tsc})_2(SO_4)]$ (light green)	m B2/b 8	25.93(4) 15.41(4) 6.61(5)	 125.0(5)	$FeO_2N_2S_2$ (cis) $FeO_2N_2S_2$ (trans)	O 2.15 N 2.16 S 2.42 O 2.12 N 2.15 S 2.42	O,O 174.72(-,3) N,N 97.63(/,0) S,S 100.88(-,0) O,N 88.25(-,43) O,S 91.68(-,3.31) N,S 80.85(-,0)[c] 175.93(-,0) O,N 94.93 O,S 92.92 N,S 82.68[c]	75
$Na[Fe^{III}(\eta^6\text{-ehpg})]\bullet 4H_2O$ (red)	or Pbcn 12	37.66(2) 7.12(1) 24.44(1)		FeO_4N_2 (cis) FeO_4N_2 (trans)	O1.976(8,109) N 2.149(9,9) O 1.967(8,63) N 2.151(9,0)	O,O 92.2(3,3.3) 112.6(3) 172.1(3) O,N 77.9(3,2)[c] 88.6(3,1.0)[d] 91.3(3,5.0) 161.7(3,7.1) N,N 79.2(3)[c] O,O 92.4(3,2.0) 107.2(3) 172.1(3) O,N 78.0(3)[c] 87.3(3)[d] 95.9(3) 167.1(3,5.0) N,N 80.6(3)[c]	76

[a]*When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e. s. d., and the second is maximum deviation from the mean*
[b]*The chemical identity of the coordinated atom or ligand is specified in these columns*
[c]*Five- membered metallocyclic ring*
[d]*Six-membered metallocyclic ring*

plus Fe-N(x2) plus Fe-Cl) bond distances are 12.78 and 12.74 Å, respectively.

Structure of another brown triclinic dimer [63] which also contain two crystallographically independent molecules, consist of well separated NEt_4^+ cations, $[Fe_2^{II,III}(\mu\text{-salmp})_2]^{1-}$ anions and dmf molecules. In this mixed – valence (Fe(II) and Fe(III)) dimer macrocyclic pentadentate salmp (3-) ligands (μ-O,O_2N_2) create a pseudo – octahedral environment around each iron atom (FeO_4N_2). In each dimeric unit the iron atoms are asymmetrically bridged by two oxygen atoms of the respective salmp(3-) ligands (Table 4). The Fe . . . Fe separations of 3.081(4) and 3.116(4) Å, rule out direct bond. The mean Fe-O-Fe and μO-Fe-μO bond angles are 94.9(4) and 85.1(4)° in molecule 1 and 96.3(3) and 83.7(3)° in molecule 2. The sum of all six (Fe-O (×4) plus Fe-N (×2)) bond distances are 12.490 and 12.484 Å, respectively.

In deep red dimer [64], two equivalent $Fe(\eta^2\text{-acac})_2$ moieties are symmetrically bridged by oxygen atoms of two OCH_2CF_3 ligands. Each iron(III) atom is octahedrally coordinated (FeO_6). The sum of all six Fe-O bond distances are 11.984 Å (molecule 1) and 12.030 Å (molecule 2) (Table 4).

X-ray analysis of colorless triclinic dimer, which also contains two crystallographically independent molecules shows [65] that the two equivalent moieties, $Fe\{\eta^3\text{-}HB(3,5\text{-}Pr^i_2pz)_3$ are held together by two μ-OH groups that are symmetrically bridged. Unfortunately, only mean values were published in the original paper. Each iron(III) atom is pentacoordinated (FeN_3O_2) (Table 4).

In structure of $[Fe_2^{III}(\mu\text{-S})_2(p\text{-mph})_4]$ [66] two Fe(p-mph)$_2$ moieties are held together by symmetrically bridged two sulfide ions. Each iron(III) atom has a distorted tetrahedral coordination (FeS_4). These two sulfide ions brings two iron atoms within 2.725(5) Å (molecule 1) and 2.722(5) Å (molecule 2), with the mean of Fe-S-Fe and

Table 7. Summary of the mean value of Fe – L (xn) (n = 4,5,6 or 7) bond distances

Compound	Chromophore	ΣFe-L(x_m) [Å] room temp.	ΣFe-L(x_m) [Å] low temp.	Ref.
Fe(II):				
Fe(η⁴-tpp)	FeN_4	7.888	7.864	77,78
[Fe(η⁴-P_4)Br]BPh_4	FeP_4Br	10.297	11.146	14
[Fe(MeCN)$_6$][$FeCl_4$]	FeN_6	13.140	12.960	79
Fe(η²-bpy)$_2$(NCS)$_2$	FeN_6	12.802	11.758	80
Fe(η²-phen)$_2$(NCS)$_2$	FeN_6	12.938	11.956	81
Fe(η²-btz)$_2$(NCS)$_2$	FeN_6	12.812	11.792	82
[Fe(η²-α-pia)$_3$](ClO_4)$_2$	FeN_6	12.224	11.948	83
[Fe(η²-α-pia)$_3$]Cl_2· $2H_2O$	FeN_6	12.036	11.982	84
[Fe(η²-α-pia)$_3$]Cl_2·EtOH[a]	FeN_6	13.170	12.450	85,86
[Fe(η²-α-pia)$_3$]Cl_2·MeOH[b]	FeN_6	12.864	12.096	87
[Fe(η²-4Mept)$_3$](ClO_4)$_2$	FeN_6	13.146	12.204	88
Fe(η⁴-tpp)(thf)$_2$	FeN_4O_2	12.930	12.848	89
[Fe(η²-dppen)$_2$$Cl_2$]2$Me_2CO$	FeP_4Cl_2	15.062	14.662	90
[Fe(η²-H_2)(H)(η²-dppe)]BPh_4	FeP_4H_3	13.334	12.123	91
Fe(III):				
[Fe(η⁴-tpp)(SPh)]PhCl	FeN_4S	10.646	10.628	92
[Fe(η⁴-tpp)(SPh)]tol	FeN_4S	10.676	10.648	92
[Fe(η⁴-tpp)(p-BrPhS)]tol	FeN_4S	10.529	10.514	92
[Fe(η⁴-oep)(2-Clpy)$_2$]ClO_4	FeN_6	12.444	12.042	93
Cs_2K[Fe(CN)$_6$]	FeC_6	11.550	11.580	94
Fe(η²-Me_2NCS_2)$_3$	FeS_6	14.376	14.036	95
Fe(η²-Me_2NCS_2)$_3$	FeS_6	14.490	13.818	96
Fe(η²-Et_2NCS_2)$_3$	FeS_6	14.148	13.836	97
Fe{η²-($C_2H_4OH)_2NCS_2$}$_3$	FeS_6	14.334	13.986	98
Fe{η²-($C_3H_4N)_2NCS_2$}$_3$	FeS_6	13.944	13.848	99
[Fe(η³-bzpa)$_2$]ClO_4	FeN_4O_2	12.022	11.608	100
[Fe(η³-acpa)$_2$]BPh_4[c]	FeN_4O_2	12.066	11.632	101
[Fe(η³-acpa)$_2$]PF_6[c]	FeN_4O_2	12.346	11.638	101
[Fe(η⁴-salen(Him)$_2$]ClO_4	FeN_4O_2	12.228	11.476	102
[Fe(η⁴-acen)(3,5-Me_2py)$_2$]BPh_4	FeN_4O_2	12.348	11.720	103
Cs[Fe(η³-tsa)$_2$]	$FeO_2N_2S_2$	13.058	13.108	104

[a]*measured at room temperature, 150 K, 115 K, and 90 K (data are at r.t. and 90 K)*
[b]*measured at 227 K, 199 K 171, K, 148 K, and 115 K (data are at 227 K and 115 K)*
[c]*measured at room temperature , 247 K, 202 K and 120 K (data are at r. t. and 120 K*

μS-Fe-μS bond angles of 75.7(2) and 104.3(3)° in the former molecule and 77.0(2) and 103.0(3)° in the latter one. The sum of all four Fe-S bond distances is 8.170 and 8.206 Å, respectively. This indicates that in the former molecule each inner coordination sphere around each iron(III) atom is somewhat more thronged than in the latter one.

In red brown [Fe_2^{II}(μ-PBu^t_2)$_2$(Me_3P)$_2$$Cl_2$] [67] two phosphorus atoms of PBu^t_2 groups serve as bridges between two Fe(Me_3P)Cl moieties, with Fe-Fe bond distances of 2.805(3) and 2.840(3) Å, respectively. Each iron(II) atom has a tetrahedral arrangement (FeP_3Cl) with different degree of distortion. The sum of (Fe-P(×3) plus Fe-Cl) bond distances are 9.419 Å in former dimer and 9.485 Å in the latter (Table 4).

Brown [Fe_2^0(μ-PPh_2)$_2$($NO)_4$] [68] contains a planar Fe_2P_2 ring. Each iron(0) atom is tetrahedrally coordinated (FeN_2P_2). There are two crystallographically independent dimers, with Fe-Fe bond distances of 2.687(1) and 2.710(2) Å, respectively.

Structure of [Fe_2^{-1}(μ-SMe)$_2$ ($NO)_4$] [69] is similar to that of [Fe_2^0(μ-PPh_2)$_2$($NO)_4$] [68]. In [69] two Fe($NO)_2$ moieties are held together by two sulfur atoms of SMe groups. The Fe-Fe bond distances are 2.686(4) and 2.700(4) Å, respectively. Each iron atom is tetrahedrally coordinated (FeN_2S_2).

There are three tetrameric species, black ($NMeEt_3$)$_3$[$Fe_4^{II/III}$(μ$_3$-S)$_4$(SPh)$_4$] which contains two – [70], black (PPh_4)$_2$[$Fe_4^{II/III}$(μ$_3$-Se)$_4$(η³-dmtb)Cl]2dmf three – [71] and dark brown (NEt_4)$_2$[Fe_4^{II}(μ-SCH_2Ph)$_6$$Br_4$] [72] two crystallographically independent molecules and their structural data are gathered in Table 4. A cubane-like framework with four triply bridging sulfur [70] or selenium [71] ligands situated above the four triangular faces of the iron tetrahedral, such that iron and sulfur or selenium atoms occupy alternate corners of a distorted cube. Structure of [$Fe_4^{II/III}$(μ$_3$-Se)$_4$(η³-dmtb)Cl]$^{2-}$ [71] is shown in Fig. 5. There are two sets of iron atoms, Fe(II) and Fe(III). The mean Fe-Fe bond distances in these mixed – valence Fe_4S_4 cores are 2.743(4) and 2.744(4) Å and in Fe_4Se_4 cores the values are 2.805(3), 2.801(3) and 2.814(3) Å. While in the former tetramer [70] each iron atom has a FeS_4 chromophore, in [71] one iron atom has $FeSe_3Cl$ and remaining three iron atoms have $FeSe_3S$ chromophores. The sum of all four (Fe-S) bond distances (molecule 1 *vs.* molecule 2) are identical 9.222 *vs.* 9.221 Å. In [71] the values for $FeSe_3Cl$ and $FeSe_3S$ (molecule 1 *vs.* molecule 2) are 9.482 and

9.482 Å *vs.* 9.430 and 9.491 Å *vs.* 9.454 and 9.504 Å.

The mean sum of Fe-L bond distances ($FeSe_3Cl$ + $FeSe_3S/2$) elongated in the order: 9.460 Å (molecule 2) < 9.479 Å (molecule 3) < 9.482 Å (molecule 1).

Structure of dark brown tetramer [72] contains well separated NEt_4^+ cations and $[Fe_4^{II}(\mu\text{-}SCH_2Ph)_6Br_6]^{2-}$ anion. The four iron(II) atoms with bridging S atoms of SCH_2Ph ligands form distorted adamantine-like core. Each iron(II) atom is tetrahedrally coordinated (FeS_3Br). The mean iron – iron separations across the sulfur bridges are 3.810 Å (molecule 1) and 3.820 Å (molecule 2).

In yellow brown derivative [73] two $Fe_3^{III}(\mu_3\text{-}O)$ units are linked across one edge via two μ-hydroxo and two pivalato ligands. There are two types of Fe(III) atoms, two of them are pentacoordinated (trigonal – bipyramidal) FeO_5 and the remaining four Fe(III) atoms are pseudo-octahedrally coordinated (FeO_6). Two crystallographically independent molecules differ mostly in the degree of distortion (Table 4). The sum of all five (Fe-O) and all six (Fe-O) bond distances (molecule 1 *vs.* molecule 2) are 9.762 and 12.005 Å *vs.* 9.763 and 11.990 Å.

The data presented in Table 4 shows that there are nine dimeric, three tetrameric and one hexameric derivatives which contain two crystallographically independent molecules within the same crystal [61–70,72,73] and one [71] which contains three such molecules. These derivatives belong to the following crystal classes: triclinic (×7), monomeric (×5) and trigonal (×1). In the dimeric derivatives iron atoms are four-, five-, and six-coordinated with the chromophores: $Fe^{III}O_3N_2$ [61], $Fe^{III}O_3N_2Cl$ [62], $Fe^{II/III}O_4N_2$ [63], $Fe^{III}O_6$ [64], $Fe^{III}N_3O_2$ [65], $Fe^{II}O_2S_2$ [66], $Fe^{II}P_3Cl$ [67], $Fe^0N_2P_2$ [68], and $Fe^{-I}N_2S_2$ [69]. In tetrameric: $Fe^{II/III}S_4$ [70], $Fe^{II/III}Se_3Cl$ (×1) plus $Fe^{II/III}Se_3S$(×3) [71], and $Fe^{II}S_3Br$ [72]. In hexameric: $Fe^{III}O_5$ (×2) plus $Fe^{III}O_6$(×4) [73].

The mean values of Fe-Fe distances and of the sum of four-, five- and six- Fe-L bond distances in the distortion isomeric derivatives, more or less crowded are summarized in Table 5. The deviation between the mean values more or less crowded, inner coordination sphere about iron atoms increase in the order: 0.023 Å (8.758 *vs.* 8.781 Å) four- < 0.027 Å (12.299 *vs.* 12.326 Å) six- < 0.071 Å (10.060 *vs.* 11.131 Å) five – coordinated.

3. Cis – trans – Isomers

There are three derivatives, $[Fe^{II}(\eta^2\text{-}\alpha\text{-}pia)_3]I_2$ [74] $[Fe^{II}(\eta^2\text{-}tsc)_2(SO_4)]$ [75] and $Na[Fe^{III}\text{-}(\eta^6\text{-}ehpg)]\bullet 4H_2O$ [76] which contain within the same crystal cis- and trans-isomeric forms and the crystallographic and structural data are gathered in Table 6. In dark red, triclinic [74] an octahedral configuration about iron(II) atom is build up by three homo – bidentate N,N' α-pia ligands (FeN_6). The mean Fe-N bond distance in cis-form of 2.063 Å is about 0.137 Å shorter than that in trans-form (2.200 Å). The five-membered metallocyclic rings with N-Fe-N bond angle of 79.9° (average) is about 4.1° more open than that found in trans-form (75.8(2)°.

In light green monoclinic $[Fe^{III}(\eta^2\text{-}tsc)_2SO_4]$ in cis form [75] two heterobidentate (N,S) thiosemicarbazides with SO_4 group created a pseudo-octahedral arrangement about each Fe(II) atom ($FeO_2N_2S_2$). The mean Fe-O, Fe-N and Fe-S bond distances (cis *vs.* trans) are 2.15, 2.16 and 2.42 Å *vs.* 2.12, 2.15 and 2.42 Å. The sum of all six Fe-L bond distance of 13.46 Å in cis – isomer is about 0.08 Å longer than those found in trans-isomer (13.38 Å).

In red orthorhombic $Na[Fe^{III}(\eta^6\text{-}ehpg)]\bullet 4H_2O$ [76] a heterohexadentate $-O_4N_2$, N,N'-ethylenebis(o-hydroxyphenylglycinate)(4-)) created about each Fe(III) atom a pseudooctahedral arrangement (FeO_4N_2). The mean Fe-O and Fe-N bond distances (cis *vs.* trans) are 1.976 and 2.1477 Å *vs.* 1.967 and 2.151 Å. The trans-isomer is somewhat more contracted than cis- isomer, with the sum of all six (Fe-O (×4) plus Fe-N(×2)) bond distances of 12.170 Å against 12.202 Å.

4. Conclusions

An analysis of almost one thousand and three hundred coordination complexes shows that some (6.7%) of them exist in isomeric forms and are summarized in this review. Included are distortions (96.6%) and cis – trans (3.4%). In coordination chemistry of iron is predominantly the chemistry of Fe(II) and Fe(III) and the isomers are not an exception. The predominant geometries are tetrahedral, square – pyramidal and pseudo – octahedral (most common). The most common ligands are with N and O donor sites.

Distortion isomerism is quite abundant in coordination complexes of iron with five derivatives existing in two isomeric forms [4–8]. There are seventy derivates which contain two crystallographically independent molecules within the same crystal [9–20,22–28,31–37,39–70,72,73] and even three such molecules [21,29,30,38,71].

The cis- and trans- isomers are present in three derivatives [74–76]. The isomers were analysed from a wide variety of the data (Fe-L bond distances, L-Fe-L metallocyclic rings, chromophores, more *vs.* less crowded inner coordination sphere) in each section and therefore will not presented here.

Many factors affecting chemical equilibrium

(total concentration, solvent, pH, molar ratio of the components, temperature, pressure, *etc.*) play an important role in the preparation of isomers. The above factors are important because they exhibit a great influence on the composition and structure of the coordination sphere in the initial reactants. The other external factors stabilizing a distorted configuration (one of many equivalent configurations) can be any weak low symmetry perturbation, *e.g.* the influence of the next (subsequent) coordination sphere, intramolecular (Van der Waals) interactions, crystal forces, hydrogen bonds, *etc.* The effect of distortion of the neighbouring moieties on a given center also represents at low symmetry perturbation. Low symmetry lead to the deformation of the complex, which in the case of weak perturbation is very small.

Special consideration is needed for distortion isomers, whose formation is conditioned by the stabilization of not one, but two or several distorted configurations. The isomer cases discussed above seem to be due to such a compromise of the "soft" properties of the iron coordination sphere and the stabilizing properties of the crystal lattice, that the various configurations so formed have nearly equal energies and therefore the isomers exist simultaneously at the same (ambient) temperature. It is necessary to emphasize the requirement of very close energy values for isomers, which is essential for the possibility of their observation at the same (or approximately the same) temperature, narrows very much the number of possible observations of distortion isomers which themselves are in thermodynamic minima.

Noticeable, there are several monomeric derivatives, which structures were measured at the different temperatures and their parameters are summarized in Table 7. There are several other derivatives [22,41,49,58–60], which were also measured at different temperatures, and therefore that contain two crystallographically independent molecules were already discussed in section 2.1. As can be seen except [14,94,104] where the sum of all five- [14] and six- [94,104] Fe-L bond distances, increase with a decreasing temperature, in all remainders (Table 4) as well as in [22,41,49,58–60] the sum reduce with lowering temperature.

Another three derivatives, $[Fe^{III}(dmso)_5Cl][Fe_2OCl_4]$ [105], $[Fe_3^{II,III}(\mu_3\text{-}O)(\mu\text{-}ac)_6(4\text{-}Etpy)_3])(4\text{-}Etpy)$ [106] and $(NBu^n)_2[Fe_4^{II,III}(\mu_3\text{-}S)_4(SPh)_4]$ [107] were also studied at different temperatures. In monomeric $[Fe^{III}(dmso)_5Cl]^{2+}$ the iron(III) is hexacoordinate (FeO_5Cl) and in $[Fe_2^{III}OCl_4]^{2-}$ each iron(III) is tetrahedrally coordinated ($FeCl_3O$). The sum of six- Fe-L bond distances and four- Fe-L bond distances are: 12.203 and 8.307 Å (at 340 K); 12.343 and 8.369 Å (at 300 K); 112.408 and 8.411 Å (at 223 K) and 12.431 and 8.466 Å (at 103 K) [105]. In [106] both Fe(II) and Fe(III) atoms are hexacoordinated (FeO_5N). The sum of the six- Fe-L bond distances are ($Fe(II)O_5N$ *vs.* $Fe(III)O_5N$) are: 12.495 *vs.* 12.306 Å (at 298 K), 12.674 *vs.* 12.274 Å (at 163 K). Finally, in [107] both Fe(II) and Fe(III) are tetrahedrally coordinated and the sum of four – Fe-L bond distances ($Fe^{II,III}S_4$) are 9.084 (at room temperature) and 9.086 Å (at 233 K) .

One of the factors affecting even inner coordination sphere around central atom is temperature. In general, the inner coordination sphere about iron atoms squeezed by lowering temperature. These examples showed that the temperature, as was mentioned above, plays an important role in observation of distortion isomers (dynamic effect).

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Abbreviations

acac	acetylacetonate
acacen	N,N-bis(acetanylethylidene)ethylenediamine(2-)
acen	ethylenebis(acetylacetoneiminate(2-)
acpa	anion of N – (1 – acetyl – 2propylidene)(2 – pyridylmethyl)amine
3-allyl-salbzen	(N-(1-acetyl-2-propylidene)(2-pyridylmethyl)aminate(1-))
[9]aneN$_3$	1, 4, 7 – triazacyclononane
[9]aneS$_3$	1, 4, 7 – trithiacyclononane
bamp	2, 6 – bis(aminomethyl)pyridine
Bu^{t}NC	tert-butyl isocyanide
bpy	2,2' – bipyridine
bta	4,4' - bithiazole

bzpa	anion of (1 – benzoylpropen – 2 – yl)(2 – pyridylmerhyl)amine
$(CH_2)_4NCS_2$	N,N – tetramethylenedithiocarbamate(1-)
$(C_2H_4OH)_2NCS_2$	N,N-bis((2-hydroxyethyl)dithiocarbamate(1-)
C_5H_{12}	pentane
$C_6H_5O_7$	citrate(3-)
$C_{42}H_{57}N_{12}O_{16}$	pseudobactrin
$C_{41}H_{64}N_9O_{17}$	siderophore
$C_{20}H_{14}N_2O_2$	2,2'-[o-phenylenebis(nitrilomethylidene)diphenolate(2-)
$C_{22}H_{25}O_5$	atrovenetin orange trimethyl ether
$C_{22}H_{26}N_4O_2$	1, 4 – piperazine(N-ethylene salicylaldiminate(2-)
$C_{31}H_{47}N_6O_{12}$	neocoprogen
3-Clpy	3-chloropyridine
5-Cl-tsa	5-chlorosalicylaldehydethiosemicarbazonate(2-)
3,5-Cl_2tsa	3,5-dichlorosalicyladehydethiosemicarbazonate(2-)
cmu	cis – methylurocanate
dipic	dipicolinate
dmf	dimethylformamide
dmso	dimethylsulphoxide
dmtb	trianion of 1, 3, 5 – tris(4, 6 – dimethyl – 3 – mercaptophenyl)thio-2, 4, 6 – tris(p – tolylthio)benzene
dpm	dipivaloylmethanate(1-)
dppe	1,2-bis(diphenylphosphine)ethane
dppen	cis-1,2-bis(diphenylphosphine)ethene
ehpg	N, N' – ethylene – bis(o-hydroxyphenylglycinate)(4-)
ens	ethylnitrosolate
Et	ethyl
Et_2NCS_2	N,N-diethyldithiocarbamate(1-)
4–Etpy	4 – ethylpyridine
$HB(3,5\text{-}Pr^i{}_2pz)_3$	hydrotris(3,5 – diisopropyl-1-pyrazolyl)borate(1-)
$HB(pz)_3$	hydrotris(1-pyrazolyl)borate(1-)
Him	imidazole
hx	hexagonal
m	monoclinic
Me	methyl
1-MeHim	1-methylimidazole
$MeBuNCS_2$	N-methyl-N-n-butyldithiocarbamate(1-)
Me_2NCS_2	N,N-dimethyldithiocarbamate(1-)
3,5-Me_2py	3,5-dimethylpyridine
mph	o – mercaptophenolate(2-)
oep	2, 3, 7, 8, 12, 13, 17, 18 – octaethylporphyrinate(2-)
3-oet-salapa	anion of Schiff base condensed from 3-ethoxysalicyladehyde with N-amino-propylaziridine
opdp	o-phenylenebis(diphenylphosphine)
$OPPh_3$	triphenylphosphineoxide
or	orthorhombic
P_4	hexaphenyl-1,4,7,10-tetraphosphadecane
PBu_2^+	di – terc - butylphosphine
Ph	phenyl
phen	1,10-phenanthroline
α-pia	2-picolylamine
Piv	pivalate(1-)
PPh_2	diphenylphosphine
$Pr^n{}_2NCS_2$	N,N-di-n-propyldithiocarbamate(1-)

py	pyridine
pyOH	2-pyridone
$S_2P(p\text{-}C_6H_4Me)_2$	di(p-tolyl)dithiophosphinate(1-)
sacsac	bis(3,5-dimethyl-1,2-dithiolium)
salen	N,N' – ethylenebis(salicylideneiminate(2-)
salmp	2-bis(salicylideneamine)methylphenolate(3-)
sane	N-(2-phenylethyl)salicylideneiminate(1-)
SPh	thiophenyl
tg	tetragonal
thf	tetrahydrofurane
tht	tetrahydrothiophene
time	2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene
tmp	5, 10, 15, 20 – tetramesitylporphyrinate(2-)
tmso	tetramethylene sulfoxide
tol	toluene
tpen	tetrakis(2-pyridylmethyl)ethylenediamine
tpp	5, 10, 15, 20 – tetraphenylporphyrinate(2-)
tppim	compound of tpp and iodoniumylides
tr	triclinic
trg	trigonal
tsalmah	N, N'-4-methyl-4-azaheptane-1,7-diylbis(thiosalicylidene-iminate(2-)
tsc	thiosemicarbazide
tttt	2, 3, 9, 10 – tetramethyl – 1, 4, 8, 11 – tetraazacyclotetradecane – 1, 3, 8, 10 – tetraene
vio	violurate

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