Chemistry of Iron with Dipicolinic Acid. 4. Mixed-Ligand Complexes of Iron(III) and Related Compounds

P. Lainé, A. Gourdon,* and J.-P. Launay

Molecular Electronics Group, CEMES, CNRS UP8011, BP4347, 29 Rue J. Marvig,
31055 Toulouse Cedex, France

Received January 27, 1995[⊗]

The chemistry of iron(III)−2,6-pyridinedicarboxylic (dipicolinic, dipicH_2) acid complexes with various ligands has been explored. Reaction of [(dipic)$Fe^{II}(OH_2)_3$] with bromine water at room temperature led to the binuclear [(dipic)(H_2O)$Fe^{III}(\mu\text{-}OH)_2Fe^{III}(OH_2)$(dipic)] complex in high yield. This dimer reacted with HX to give [(dipic)(X)$Fe^{III}(OH_2)_2$] (X = Br or Cl (**1**)). Reaction of **1** with 2,4-pentanedione (acacH) yielded [(dipic)(acac)$Fe^{III}(OH_2)$] (**2**), and reaction with 1,10-phenanthroline (phen) gave [(dipic)(Cl)Fe^{III}(phen)] (**3**). The reaction of [(dipic)$Fe^{II}(OH_2)_3$] with polypyridyl tridentate ligands L did not yield [(dipic)Fe^{II}(L)] but $[Fe^{II}L_2]^{2+}$ with $[(\text{dipic})_2Fe^{III}]^-$ as counterions. For instance, with L = 2,2′:6′,2″-terpyridine (tpy), the reaction gave $[Fe^{II}(\text{tpy})_2][(\text{dipic})_2Fe^{III}]_2$ (**4**) and with L = tetrakis(2-pyridyl)pyrazine (tppz) it gave $\{[Fe^{II}(\text{tppz})_2][(\text{dipic})_2Fe^{III}]_3\}\cdot(H_3O)$ (**5**). The crystallographic structures of **1**−**5** have been solved: **1**, monoclinic, *C*2/*c*, *a* = 6.015(6) Å, *b* = 18.74(1) Å, *c* = 9.81(1) Å, β = 105.5(6) °, *V* = 1062(2) Å^3, *Z* = 4; **2**·0.5C_2H_5OH, monoclinic, *C*2/*c*, *a* = 11.510(3) Å, *b* = 12.734(4) Å, *c* = 21.819(4) Å, β = 98.27(2)°, *V* = 3165(7) Å^3, *Z* = 8; **3**·CH_2Cl_2, monoclinic, *P*2$_1$/*n*, *a* = 9.083(2) Å, *b* = 12.899(2) Å, *c* = 17.490(4) Å, β = 96.70(8)°, *V* = 2035(2) Å^3, *Z* = 4; **4**·H_2O·3CH_3CN, monoclinic, *P*2$_1$/*n*, *a* = 8.947(2) Å, *b* = 37.37(2) Å, *c* = 18.97(2) Å, β = 100.07(8)°, *V* = 6243(8) Å^3, *Z* = 4; **5**·11H_2O, monoclinic, *C*2/*c*, *a* = 32.46(3) Å, *b* = 28.30 Å, *c* = 27.59(2) Å, β = 126.34(6)°, *V* = 20417 Å^3 and *Z* = 8.

Introduction

In the previous papers of this series, we have seen the great diversity of possible structures for iron(II)−dipicolinate complexes. We now turn to the case of iron(III) compounds. Besides their applications[1] in domains such as biochemistry, analytical chemistry, and catalysis, they could be used for our purpose as precursors for bridged binuclear complexes. For instance, a mono(dipicolinate) complex such as $[(\text{dipic})Fe^{III}L_3]^+$ with labile L_3 would allow the synthesis of bridged compounds of the type [(dipic)Fe(dipic−R−dipic)Fe(dipic)]. We have also considered the case of complexes of general formula [(dipic)Fe^{III}L(AA)] where AA is a chelating ligand and L a labile molecule, which could be substituted by a bis-monodentate bridging ligand.

Experimental Section

Most of the experimental details have been reported in ref 1. Magnetic measurements were performed on a Faraday balance at constant magnetic field (1000 G) and constant gradient (500 G cm^{-1}). Diamagnetic corrections were applied using Pascal's constants.[2]

Synthesis of [(dipic)(H_2O)$Fe^{III}(\mu\text{-}OH)_2Fe^{III}(OH_2)$(dipic)]. Bromine water (3.3 × 10^{-2} M) was added dropwise to a solution of [(dipic)$Fe^{II}(OH_2)_3$] (688 mg, 2.50 mmol) in water (250 mL). Upon addition, the initially deep orange solution bleached with the appearance of a pale green precipitate. When the reaction mixture was colorless, addition was stopped (pH 2.30) and the precipitate was filtered off, washed with ethanol and diethyl ether, and air-dried. Yield: 591 mg, 92%. Anal. Calcd for $C_{14}H_{12}N_2Fe_2O_{12}$: C, 32.84; H, 2.36; N, 5.47; Fe, 21.82. Found: C, 32.86; H, 2.37; N, 5.48; Fe, 21.83. FTIR (KBr, cm^{-1}): 3407, 2927 (ν_{sym} O−H); 1658, 1625, 1578 (ν_{asym} COO^-); 1437 (ν_{sym} COO^-).

Synthesis of [(dipic)(Br)$Fe^{III}(OH_2)_2$]. Method a. Pure Bromine was carefully added dropwise to a solution of [(dipic)$Fe^{II}(OH_2)_3$] (1.376 g, 5 mmol) in hot water (95 °C, 50 mL). Upon addition, the initially deep orange solution bleached with apparition of a pale green precipitate which partially dissolved and the solution turned orange brown. The addition was stopped at pH 1.5. The precipitate was filtered off, giving 629 mg of $[(\text{dipic})Fe^{III}(\mu\text{-}OH)(OH_2)]_2$ (yield 49%). The orange filtrate was concentrated to 10 mL under vacuum and left for 48 h at 4 °C, yielding brown needles of [(dipic)(Br)$Fe^{III}(OH_2)_2$] (716 mg, 42%). Anal. Calcd for $C_7H_7NFeO_6Br$: C, 24.96; H, 2.09; N, 4.16; Br, 23.72; Fe, 16.58. Found: C, 25.06; H, 2.10; N, 4.14; Br, 23.85; Fe, 16.47.

Method b. A suspension (2 g, 3.9 mmol) of $[(\text{dipic})(H_2O)Fe^{III}(\mu\text{-}OH)]_2$ in 40 mL of aqueous 0.1 M HBr was heated at 95 °C until complete dissolution. The brown solution was then concentrated to 25 mL and left to cool to room temperature. Yield: 1.118 g, 85%. FTIR (KBr, cm^{-1}): 3101 (ν_{sym} O−H); 1667, 1596 (ν_{asym} COO^-); 1468, 1429 (ν_{sym} COO^-). UV−vis in MeOH, 1 M (TBA)Br (λ_{max}, nm ($10^{-2}\epsilon$, dm^3 mol^{-1} cm^{-1})): 371.5 (29.30) (LMCT Br^-).

Synthesis of [(dipic)(Cl)$Fe^{III}(OH_2)_2$] (1). A suspension (600 mg, 1.17 mmol) of $[(\text{dipic})(H_2O)Fe^{III}(\mu\text{-}OH)]_2$ in 40 mL of aqueous 0.1 M HCl was heated at 95 °C until complete dissolution of the solid. The green-yellow solution was then concentrated to 7 mL and left to cool to room temperature. Yield: 495 mg, 72%. FTIR (KBr, cm^{-1}): 3101 (ν_{sym} O−H); 1667, 1596 (ν_{asym} COO^-); 1468, 1429 (ν_{sym} COO^-). UV−vis in MeOH (λ_{max}, nm ($10^{-2}\epsilon$, dm^3 mol^{-1} cm^{-1})): 314 (62.45) (LMCT Cl^-).

Synthesis of [(dipic)(acac)Fe^{III}(S)] (2: S = Solvent H_2O). Method a.[3] A hot solution of dipicH_2 (0.8379 g, 5 mmol) in 100 mL of ethanol was added to a solution of $[(\text{acac})_3Fe^{III}]$[4] (1.765 g, 5 mmol) in 50 mL of ethanol. The solution was refluxed for 20 h, concentrated to 30 mL, and cooled. Addition of diethyl ether precipitated the crude product. The precipitate was washed with diethyl ether and dissolved

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1995.

(1) Lainé, P.; Gourdon, A.; Launay, J.-P. *Inorg. Chem.* **1995**, *34*, 5129 and references therein.

(2) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin Heidelberg, 1986; p 3.

(3) (a) Hoof, D. L.; Walton, R. A. *Inorg. Chim. Acta* **1975**, *12*, 71. (b) Aly, M. M.; El-Awad, M. *Inorg. Chim. Acta* **1980**, *38*, 3. Both references describe the same preparation conditions but with stoichiometries dipicH_2:Fe = 2:1 for ref a and dipicH_2:Fe = 1 for ref b.

(4) Chaudhuri, M. K.; Ghosh, S. K. *J. Chem. Soc., Dalton Trans.* **1983**, *4*, 839.

0020-1669/95/1334-5156$09.00/0

Table 1. Crystal Data for [(dipic)(Cl)Fe^{III}(OH$_2$)$_2$] (**1**), [(dipic)(acac)Fe^{III}(OH$_2$)]·0.5C$_2$H$_5$OH (**2**), [(dipic)(Cl)Fe^{III}(phen)]·CH$_2$Cl$_2$ (**3**), [Fe^{II}(tpy)$_2$][(dipic)$_2$Fe^{III}]$_2$·H$_2$O·3CH$_3$CN (**4**), and [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_3$·H$_3$O·11H$_2$O (**5**)

	1	**2**	**3**	**4**	**5**
formula	$C_7H_7NClFeO_6$	$C_{12}H_{12}NFeO_7$	$C_{20}H_{13}N_3Cl_3FeO_4$	$C_{58}H_{42}N_{10}Fe_3O_{20}$	$C_{90}H_{75}N_{18}Fe_4O_{36}$
fw	292.435	337.08	521.55	1366.57	2208.07
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*P*2$_1$/*n* (No. 14)	*P*2$_1$/*n* (No. 14)	*C*2/*c* (No. 15)
a, Å	6.015(6)	11.510(3)	9.083(2)	8.947(2)	32.46(3)
b, Å	18.74(1)	12.734(4)	12.899(2)	37.37(2)	28.30(1)
c, Å	9.81(1)	21.819(4)	17.490(4)	18.97(2)	27.59(2)
β, deg	105.05(6)	98.27(2)	96.70(8)	100.07(8)	126.34(6)
V, Å^3	1068(2)	3165(7)	2035(2)	6243(8)	20417(30)
Z	4	8	4	4	8
T, °C	21	21	21	21	21
μ(Mo Kα), cm^{-1}	16.72	8.83	11.70	7.67	6.44
ϱ_{calcd}, g cm^{-3}	1.82	1.49	1.70	1.53	1.437
R^a	0.032	0.035	0.030	0.052	0.097
$R_w{}^b$	0.037	0.042	0.035	0.058	0.107

$^a\, R = \Sigma|/|F_o| - |F_c||/\Sigma|F_o|$. $^b\, R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

in dry ethanol. The white residue (dipicH$_2$) was then filtered off, and the filtrate was concentrated under vacuum to 20 mL and left at 4 °C, giving 655 mg (yield 38%) of purplish-blue crystals suitable for X-ray crystallography.

Method b. To a suspension of [(dipic)(H$_2$O)Fe^{III}(μ-OH)]$_2$ (495 mg, 0.97 mmol) in 25 mL of ethanol was added 0.2 mL of acetylacetone (1.95 mmol), and the mixture was refluxed 4 h. The orange-red solution was left to cool to room temperature. Ether was then added up to the cloud point and the solution was stored at 4 °C for 1 week. The crystals were then filtered off, washed with diethyl ether, and air-dried (615 mg, 94%).

Method c. A suspension of [(dipic)(Cl)Fe^{III}(OH$_2$)$_2$] (570 mg, 1.95 mmol) was refluxed in 60 mL of ethanol for a few minutes. Then 10 mL of an ethanolic solution of acetylacetone (0.3 mL, 2.92 mmol) was added dropwise, and the mixture was stirred for 10 h at room temperature. The product was precipitated by addition of diethyl ether, filtered off, and washed with diethyl ether (585 mg, 89%). Anal. Calcd for [(dipic)(acac)Fe^{III}(OH$_2$)]: C, 42.63; H, 3.57; N, 4.14; Fe, 16.52. Found: C, 42.63; H, 3.67; N, 4.24; Fe, 16.23. FTIR (KBr, cm^{-1}): 3433, 3089, 2970 (ν_{sym} O–H); 1660, 1630 (ν_{asym} COO); 1562 (ν_{sym} C–O$_{acac^-}$); 1533 (ν_{sym} C–C$_{acac^-}$); 1433 (ν_{sym} COO). UV–vis in ethanol (λ_{max}, nm ($10^{-2}\epsilon$, dm^3 mol^{-1} cm^{-1})): 445(14) (LMCT acac$^-$); 347 (19) sh (LMCT acac$^-$); 271 (195) (nπ^*).

Synthesis of [(dipic)(Cl)Fe^{III}(phen)] (3) (phen = 1,10-Phenanthroline). A solution of 1,10-phenanthroline hydrate (700 mg, 3.53 mmol) in acetonitrile (20 mL) was added to a suspension of [(dipic)(Cl)Fe^{III}(OH$_2$)$_2$] (1.02 g, 3.49 mmol) in acetonitrile (80 mL). The mixture was stirred for 12 h at room temperature and then filtered. The deep yellow precipitate was washed with diethyl ether, dried, and recrystallized by slow evaporation of a saturated solution in dichloromethane (yield 1.38 g, 90%). The compound must be stored in the cold under argon. Anal. Calcd for $C_{19}H_{11}N_3FeO_4Cl$: C, 52.27; H, 2.54; N, 9.62; Cl, 8.20; Fe, 12.79. Found: C, 51.94; H, 2.70; N, 9.58; Cl, 8.17; Fe, 12.64. The synthesis was also done in a similar way in ethanol, with a final recrystallization in acetonitrile. The chemical analysis was consistent with the monohydrate: [(dipic)(Cl)Fe^{III}(phen)]·H$_2$O. Anal. Calcd for $C_{19}H_{13}N_3FeO_5Cl$: C, 50.20; H, 2.88; N, 9.24; Cl, 7.79; Fe, 12.28. Found: C, 50.26; H, 2.92; N, 9.25; Cl, 7.84; Fe, 12.16. FTIR (KBr, cm^{-1}): 3437 w (ν_{sym} O–H); 1668, 1584 (ν_{asym} COO); 1465, 1427 (ν_{sym} COO). UV–vis in CH$_2$Cl$_2$ (λ_{max}, nm ($10^{-2}\epsilon$, dm^3 mol^{-1} cm^{-1})): 322 (6.2) (LMCT, Cl$^-$); 269 (355) (nπ^*); 224 (522.6) ($\pi\pi^*$).

Synthesis of [(dipic)(Br)Fe^{III}(phen)]. A solution of 1,10-phenanthroline hydrate (181 mg, 0.91 mmol) in dichloromethane (20 mL) was added dropwise to a suspension of [(dipic)(Br)Fe^{III}(OH$_2$)$_2$] (300 mg, 0.89 mmol) in dichloromethane (180 mL). The mixture was then stirred 12 h at room temperature and filtered, and the orange-brown precipitate was washed with diethyl ether and air-dried. Yield: 376 mg, 88%. The product must be stored under argon in the cold. FTIR (KBr, cm^{-1}): 3437 w (ν_{sym} O–H); 1668, 1584 (ν_{asym} COO); 1465, 1427 (ν_{sym} COO). UV–vis in CH$_2$Cl$_2$ (λ_{max}, nm ($10^{-2}\epsilon$, dm^3 mol^{-1} cm^{-1})): 406 (20.1) (LMCT, Br$^-$); 269 (352) (nπ^*); 224 (403) ($\pi\pi^*$).

Synthesis of [Fe^{II}(phen)$_3$][(dipic)$_2$Fe^{III}]$_2$·3H$_2$O. a. By Thermal Degradation of [(dipic)(Cl)Fe^{III}(phen)]. A solution of [(dipic)(Cl)Fe^{III}(phen)] (250 mg, 5.72 mmol) was refuxed for 48 h in 400 mL of acetonitrile. The initially yellow solution turned orange and then purplish-red with apparition of red crystals. Slow cooling of the solution yielded crystals, which were filtered off, and washed with diethyl ether. Anal. Calcd for [Fe^{II}(phen)$_3$][(dipic)$_2$Fe^{III}]$_2$·3H$_2$O ($C_{64}H_{42}N_{10}Fe_3O_{19}$): C, 54.03; H, 2.97; N, 9.84; Fe, 11.77. Found: C, 53.92; H, 3.21; N, 9.91; Fe, 11.65.

b. Directly from [(dipic)Fe^{II}(OH$_2$)$_3$]. To a suspension of [(dipic)Fe^{II}(OH$_2$)$_3$] (504 mg, 1.83 mmol) in dichloromethane (200 mL) was added a solution of 1,10-phenanthroline (328 mg, 1.82 mmol) in dichloromethane (20 mL), and the mixture was stirred for 48 h. Extraction of the precipitate with acetonitrile gave 75 mg of violet powder after removal of solvent. Futher extraction of the residue (Soxhlet; acetonitrile, 3 days) gave a dark red powder of [Fe^{II}(phen)$_3$][(dipic)$_2$Fe^{III}]$_2$·3H$_2$O (305 mg, yield 35%). Anal. Calcd for [Fe^{II}(phen)$_3$][(dipic)$_2$Fe^{III}]$_2$·3H$_2$O ($C_{64}H_{42}N_{10}Fe_3O_{19}$): C, 54.03; H, 2.97; N, 9.84; Fe, 11.77. Found: C, 54.06; H, 3.01; N, 9.85; Fe, 11.86. FTIR (KBr, cm^{-1}): 3433 w (ν_{sym} O–H); 1671, 1595 (ν_{asym} COO); 1471, 1427 (ν_{sym} COO). UV–vis in CH$_3$CN (λ_{max}, nm ($10^{-2}\epsilon$, dm^3 mol^{-1} cm^{-1})): 511 (29.45) (MLCT); 267 (289) (nπ^*); 223 (353) ($\pi\pi^*$).

Synthesis of [Fe^{II}(tpy)$_2$][(dipic)$_2$Fe^{III}]$_2$ (4) (tpy = Terpyridine). To a solution of terpyridine (100 mg, 0.43 mmol) in ethanol (100 mL) was added a large excess of [(dipic)Fe^{II}(OH$_2$)$_3$] (500 mg, 1.82 mmol). After 24 h of stirring at room temperature, the residual insoluble [(dipic)Fe^{II}(OH$_2$)$_3$] was filtered off and the deep blue-violet solution was rotoevaporated. The solid residue was then extracted with acetonitrile and recrystallized in this solvent. Yield: 250 mg, 84% vs tpy. Anal. Calcd for [Fe^{II}(tpy)$_2$][(dipic)$_2$Fe^{III}]$_2$·4H$_2$O (before recrystallization) ($C_{58}H_{42}N_{10}Fe_3O_{20}$): C, 50.97; H, 3.09; N, 10.25; Fe, 12.26. Found: C, 50.66; H, 3.10; N, 10.19; Fe, 11.56. FTIR (KBr, cm^{-1}): 1674, 1632 (ν_{asym} COO); 1431 (ν_{asym} COO).

Synthesis of [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_2$ (tppz = Tetrapyridylpyrazine). A large excess of [(dipic)Fe^{II}(OH$_2$)$_3$] (570 mg, 2.07 mmol) was added to a boiling solution of tppz (200 mg, 0.51 mmol) in acetonitrile (200 mL). The mixture was stirred for 24 h at 50 °C and filtered, and the filtrate was rotoevaporated. The residue was then extracted with a Soxhlet apparatus during 3 days. Anal. Calcd for [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_2$·6H$_2$O ($C_{76}H_{56}N_{16}Fe_3O_{22}$): C, 53.29; H, 3.29; N, 13.09; Fe, 9.78. Found: C, 53.43; H, 3.25; N, 12.76; Fe, 9.68. Recrystallization by slow evaporation of an aqueous solution induced partial decomposition of this product and gave another salt: [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_3$·H$_3$O·11H$_2$O (**5**), as shown by X-ray crystallography.

X-ray Crystallography. Experimental apparatus, procedures, and computer programs are as in ref 1. Crystal data and data collection details are given in Table 1. Selected atomic coordinates are given in Tables 2, 4, 6, 8, and 10; selected bond lengths and angles are grouped in Tables 3, 5, 7, 9, and 11.

Table 2. Selected Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for [(dipic)(Cl)Fe^{III}(OH$_2$)$_2$] (**1**)

atom	*x/a*	*y/b*	*z/c*	*U*(iso)[a]
Fe(1)	0.0000	−0.02815(2)	0.2500	0.0201
Cl(1)	0.0000	0.09012(5)	0.2500	0.0407
N(1)	0.0000	−0.1383(1)	0.2500	0.0199
C(1)	0.2795(4)	−0.1208(1)	0.1254(2)	0.0218
C(2)	0.1391(4)	−0.1726(1)	0.1864(2)	0.0220
C(3)	0.1455(5)	−0.2462(1)	0.1847(3)	0.0314
C(4)	0.0000	−0.2828(2)	0.2500	0.0360
O(11)	0.2321(3)	−0.05456(9)	0.1404(2)	0.0233
O(12)	0.4291(3)	−0.1417(1)	0.0700(2)	0.0275
O(110)	−0.2590(3)	−0.0362(1)	0.0684(2)	0.0303

[a] Equivalent isotropic *U*(iso) defined as one-third of the trace of the orthogonalized tensor.

Table 3. Selected Bond Distances and Angles for [(dipic)(Cl)Fe^{III}(OH$_2$)$_2$] (**1**)

Fe(1)−Cl(1)	2.217(1)	Fe(1)−O(110)	2.046(2)
Fe(1)−N(1)	2.066(3)	C(1)−O(11)	1.291(3)
Fe(1)−O(11)	2.032(2)	C(1)−O(12)	1.229(3)
O(11)−Fe(1)−Cl(1)	104.10(5)	O(110)−Fe(1)−N(1)	85.76(6)
O(11)−Fe(1)−N(1)	75.90(5)	O(110)−Fe(1)−O(11)	89.62(7)
O(11)−Fe(1)−O(11)′	151.80(9)	O(110)−Fe(1)−O(11)′	88.32(7)
O(110)−Fe(1)−Cl(1)	94.24(6)	O(110)−Fe(1)−O(110)′	171.5(1)

Table 4. Selected Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for [(dipic)(acac)Fe^{III}(OH$_2$)]·0.5C$_2$H$_5$OH (**2**)

atom	*x/a*	*y/b*	*z/c*	*U*(iso)[a]
Fe(1)	0.11428(3)	0.09607(2)	0.12575(2)	0.0314
O(110)	−0.0522(2)	0.0460(2)	0.11633(9)	0.0385
N(1)	0.1808(2)	−0.0539(1)	0.14191(9)	0.0296
C(1)	0.1775(2)	−0.0508(2)	0.0344(1)	0.0339
C(2)	0.2066(2)	−0.1100(2)	0.0944(1)	0.0317
C(3)	0.2520(3)	−0.2099(2)	0.1036(1)	0.0446
C(4)	0.2677(3)	−0.2490(2)	0.1634(2)	0.0498
C(5)	0.2377(3)	−0.1903(2)	0.2122(1)	0.0463
C(6)	0.1944(2)	−0.0907(2)	0.1990(1)	0.0335
C(7)	0.1555(2)	−0.0113(2)	0.2433(1)	0.0363
O(11)	0.1347(2)	0.0405(1)	0.03995(8)	0.0370
O(12)	0.1956(2)	−0.0920(2)	−0.01422(8)	0.0436
O(71)	0.1233(2)	0.0766(1)	0.21890(8)	0.0383
O(72)	0.1570(2)	−0.0361(2)	0.29779(9)	0.0508
O(121)	0.0551(2)	0.2337(2)	0.0997(1)	0.0525
O(141)	0.2732(2)	0.1584(2)	0.1359(1)	0.0524
C(11)	0.0353(6)	0.3951(4)	0.0479(4)	0.1072
C(12)	0.1090(3)	0.3065(2)	0.0755(2)	0.0632
C(13)	0.2274(3)	0.3096(3)	0.0762(2)	0.0620
C(14)	0.3043(3)	0.2393(3)	0.1066(2)	0.0546
C(15)	0.4327(4)	0.2547(4)	0.1089(3)	0.0877
O(211)	0.5000	0.029(2)	0.2500	0.093(5)
C(21)	0.509(3)	−0.045(2)	0.216(1)	0.126(9)
C(22)	0.457(4)	0.005(3)	0.164(2)	0.17(1)
O(311)	0.523(2)	0.005(2)	0.206(1)	0.165(9)
C(31)	0.5000	0.094(3)	0.2500	0.16(2)
C(32)	0.414(2)	0.081(2)	0.256(1)	0.113(7)

[a] Equivalent isotropic *U*(iso) defined as one-third of the trace of the orthogonalized tensor.

[(dipic)(Cl)Fe^{III}(OH$_2$)$_2$] crystallizes in the centrosymmetric space group *C*2/*c* with half a molecule per asymmetric unit. The iron atom lies on a binary crystallographic axis going through H(4), C(4), N(1), and Cl(1).

[(dipic)(acac)Fe^{III}(OH$_2$)]·0.5C$_2$H$_5$OH crystallizes in the centrosymmetric space group *C*2/*c*. The asymmetric unit contains half a molecule of ethanol disordered around the binary axis. The coordinates of the atoms of this solvate were refined with slack constraints, with fixed temperature factors of 0.05 Å^2, and with free occupation factors which converged to 0.25, a value to which they were fixed in the next steps of the refinement. The hydrogen atoms of this molecule were not found.

Table 5. Selected Bond Distances (Å) and Angles (deg) for [(dipic)(acac)Fe^{III}(OH$_2$)]·0.5C$_2$H$_5$OH (**2**)

Fe(1)−O(110)	2.002(2)	C(1)−O(12)	1.228(3)
Fe(1)−N(1)	2.069(2)	C(7)−O(71)	1.272(3)
Fe(1)−O(11)	2.046(2)	C(7)−O(72)	1.228(3)
Fe(1)−O(71)	2.035(2)	O(121)−C(12)	1.271(4)
Fe(1)−O(121)	1.935(2)	O(141)−C(14)	1.290(4)
Fe(1)−O(141)	1.977(2)	O(211)−C(21)	1.22(3)
C(1)−O(11)	1.275(3)	O(311)−C(31)	1.53(3)
N(1)−Fe(1)−O(110)	92.79(8)	O(121)−Fe(1)−O(11)	97.26(9)
O(11)−Fe(1)−O(110)	91.74(8)	O(121)−Fe(1)−O(71)	111.62(9)
O(11)−Fe(1)−N(1)	75.42(7)	O(141)−Fe(1)−O(110)	174.86(8)
O(71)−Fe(1)−O(110)	88.53(8)	O(141)−Fe(1)−N(1)	92.16(8)
O(71)−Fe(1)−N(1)	75.71(7)	O(141)−Fe(1)−O(11)	90.87(9)
O(71)−Fe(1)−O(11)	151.11(7)	O(141)−Fe(1)−O(71)	91.33(9)
O(121)−Fe(1)−O(110)	88.12(8)	O(141)−Fe(1)−O(121)	87.15(9)
O(121)−Fe(1)−N(1)	172.64(9)		

Table 6. Selected Positional and Equivalent Isotropic Thermal Parameters (Å^2) for [(dipic)(Cl)Fe^{III}(phen)]·CH$_2$Cl$_2$ (**3**)

atom	*x/a*	*y/b*	*z/c*	*U*(iso)[a]
Fe(1)	0.23302(3)	0.27064(2)	0.50389(2)	0.0310
Cl(1)	0.06879(7)	0.29620(5)	0.39893(3)	0.0476
N(1)	0.2020(2)	0.1158(1)	0.5261(1)	0.0312
C(1)	0.0385(2)	0.1840(2)	0.6075(1)	0.0375
C(2)	0.1122(2)	0.0897(2)	0.5779(1)	0.0331
C(3)	0.0929(3)	−0.0131(2)	0.5959(1)	0.0383
C(4)	0.1654(3)	−0.0877(2)	0.5571(1)	0.0396
C(5)	0.2550(2)	−0.0588(2)	0.5018(1)	0.0372
C(6)	0.2728(2)	0.0454(2)	0.4886(1)	0.0323
C(7)	0.3678(2)	0.0956(2)	0.4338(1)	0.0364
O(11)	0.0852(2)	0.2705(1)	0.58086(9)	0.0386
O(12)	−0.0581(2)	0.1754(2)	0.6496(1)	0.0506
O(71)	0.3750(2)	0.1953(1)	0.4397(1)	0.0385
O(72)	0.4293(2)	0.0427(1)	0.3896(1)	0.0499
N(2)	0.2822(2)	0.4330(1)	0.5178(1)	0.0337
N(3)	0.4173(2)	0.2771(1)	0.5961(1)	0.0328
C(21)	0.2116(3)	0.5097(2)	0.4773(2)	0.0420
C(22)	0.2446(3)	0.6147(2)	0.4934(2)	0.0467
C(23)	0.3493(3)	0.6391(2)	0.5526(2)	0.0441
C(24)	0.4242(3)	0.5604(2)	0.5969(1)	0.0384
C(25)	0.3858(2)	0.4579(2)	0.5765(1)	0.0316
C(26)	0.4592(2)	0.3738(2)	0.6190(1)	0.0319
C(27)	0.5674(3)	0.3947(2)	0.6805(1)	0.0411
C(28)	0.6364(3)	0.3087(2)	0.7190(2)	0.0490
C(29)	0.5954(3)	0.2113(2)	0.6951(2)	0.0506
C(30)	0.4853(3)	0.1977(2)	0.6338(1)	0.0422
C(31)	0.5334(3)	0.5793(2)	0.6607(2)	0.0483
C(32)	0.6016(3)	0.5002(2)	0.7007(2)	0.0492

[a] Equivalent isotropic *U*(iso) defined as one-third of the trace of the orthogonalized tensor.

Table 7. Selected Bond Distances (Å) and Angles (deg) for [(dipic)(Cl)Fe^{III}(phen)]·CH$_2$Cl$_2$ (**3**)

Fe(1)−Cl(1)	2.2506(7)	C(1)−O(11)	1.299(3)
Fe(1)−N(1)	2.060(2)	C(1)−O(12)	1.214(3)
Fe(1)−O(11)	2.009(1)	C(7)−O(71)	1.292(3)
Fe(1)−O(71)	2.050(2)	C(7)−O(72)	1.215(3)
Fe(1)−N(2)	2.149(2)	Cl(101)−C(100)	1.755(3)
Fe(1)−N(3)	2.186(2)	Cl(102)−C(100)	1.746(4)
N(1)−Fe(1)−Cl(1)	101.75(5)	N(2)−Fe(1)−O(11)	94.12(7)
O(11)−Fe(1)−Cl(1)	96.64(5)	N(2)−Fe(1)−O(71)	112.82(6)
O(11)−Fe(1)−N(1)	75.87(7)	N(3)−Fe(1)−Cl(1)	166.82(5)
O(71)−Fe(1)−Cl(1)	91.28(5)	N(3)−Fe(1)−N(1)	90.44(7)
O(71)−Fe(1)−N(1)	75.65(6)	N(3)−Fe(1)−O(11)	91.15(6)
O(71)−Fe(1)−O(11)	151.43(6)	N(3)−Fe(1)−O(71)	86.86(7)
N(2)−Fe(1)−Cl(1)	93.36(5)	N(3)−Fe(1)−N(2)	75.43(7)
N(2)−Fe(1)−N(1)	162.66(7)	Cl(102)−C(100)−Cl(101)	111.7(2)

[(dipic)(Cl)Fe^{III}(phen)] cocrystallizes in the space group *P*2$_1$/*n* with one molecule of dichloromethane. All the atoms of this solvent were localized on Fourier maps, and their coordinates were refined.

Table 8. Selected Positional and Equivalent Isotropic Thermal Parameters (Å^2) for $[Fe^{II}(tpy)_2][(dipic)_2Fe^{III}]_2 \cdot H_2O \cdot 3CH_3CN$ (**4**)

atom	*x/a*	*y/b*	*z/c*	*U*(iso)[a]	atom	*x/a*	*y/b*	*z/c*	*U*(iso)[a]
Fe(1)	0.3858(1)	0.19430(3)	0.30673(6)	0.0490	C(36)	0.411(1)	0.4399(3)	0.4412(4)	0.0544
N(1)	0.3503(6)	0.1621(1)	0.2171(3)	0.0419	C(37)	0.482(1)	0.4030(3)	0.4463(5)	0.0735
C(1)	0.5337(9)	0.1273(2)	0.2905(4)	0.0514	O(311)	0.1797(6)	0.4423(2)	0.5928(3)	0.0682
C(2)	0.4310(8)	0.1324(2)	0.2181(4)	0.0437	O(312)	0.1017(8)	0.4985(2)	0.5798(4)	0.0839
C(3)	0.4182(9)	0.1108(2)	0.1581(4)	0.0508	O(371)	0.4538(6)	0.3856(2)	0.5000(3)	0.0683
C(4)	0.3174(9)	0.1210(2)	0.0986(4)	0.0521	O(372)	0.5565(9)	0.3926(3)	0.4023(4)	0.1103
C(5)	0.2312(8)	0.1515(2)	0.0982(4)	0.0507	Fe(3)	0.6461(1)	0.38173(3)	0.16252(5)	0.0368
C(6)	0.2526(8)	0.1719(2)	0.1595(4)	0.0447	N(100)	0.6293(6)	0.4307(1)	0.1815(3)	0.0347
C(7)	0.1742(9)	0.2062(2)	0.1722(5)	0.0587	C(101)	0.7018(7)	0.4440(2)	0.2447(3)	0.0378
O(11)	0.5230(6)	0.1524(1)	0.3353(3)	0.0581	C(102)	0.6909(9)	0.4796(2)	0.2596(4)	0.0573
O(12)	0.6156(7)	0.1010(2)	0.3012(3)	0.0700	C(103)	0.604(1)	0.5015(2)	0.2106(5)	0.0637
O(71)	0.2216(6)	0.2203(1)	0.2347(3)	0.0618	C(104)	0.532(1)	0.4879(2)	0.1457(4)	0.0573
O(72)	0.0746(8)	0.2191(2)	0.1266(3)	0.0842	C(105)	0.5450(8)	0.4518(2)	0.1324(4)	0.0410
N(11)	0.3887(6)	0.2376(2)	0.3737(3)	0.0421	N(110)	0.7646(6)	0.3824(2)	0.2602(3)	0.0395
C(11)	0.5884(9)	0.2555(2)	0.3166(4)	0.0490	C(111)	0.8322(8)	0.3551(2)	0.2992(4)	0.0500
C(12)	0.4781(7)	0.2653(2)	0.3665(4)	0.0385	C(112)	0.9187(9)	0.3592(2)	0.3659(4)	0.0575
C(13)	0.4674(8)	0.2973(2)	0.4012(4)	0.0479	C(113)	0.9398(9)	0.3924(3)	0.3949(4)	0.0611
C(14)	0.3566(9)	0.2991(2)	0.4439(4)	0.0544	C(114)	0.8700(9)	0.4215(2)	0.3564(4)	0.0588
C(15)	0.2612(8)	0.2705(2)	0.4516(4)	0.0510	C(115)	0.7839(7)	0.4155(2)	0.2896(4)	0.0397
C(16)	0.2826(8)	0.2397(2)	0.4147(4)	0.0449	N(150)	0.5222(6)	0.3966(2)	0.0701(3)	0.0379
C(17)	0.1957(9)	0.2044(2)	0.4130(4)	0.0526	C(151)	0.4764(8)	0.3758(2)	0.0128(4)	0.0487
O(111)	0.5580(6)	0.2255(1)	0.2846(3)	0.0536	C(152)	0.3838(9)	0.3891(3)	−0.0478(4)	0.0598
O(112)	0.6916(6)	0.2755(1)	0.3092(3)	0.0582	C(153)	0.3421(9)	0.4242(3)	−0.0500(4)	0.0589
O(171)	0.2389(6)	0.1812(1)	0.3701(3)	0.0569	C(154)	0.3894(9)	0.4460(2)	0.0083(4)	0.0581
O(172)	0.0975(7)	0.2007(2)	0.4483(3)	0.0717	C(155)	0.4824(7)	0.4313(2)	0.0675(4)	0.0399
Fe(2)	0.3288(1)	0.40598(3)	0.56795(6)	0.0502	N(200)	0.6635(8)	0.3327(2)	0.1426(3)	0.0504
N(21)	0.3568(6)	0.3732(1)	0.6558(3)	0.0377	C(201)	0.789(1)	0.3218(3)	0.1160(4)	0.0547
C(21)	0.5448(8)	0.4149(2)	0.6996(4)	0.0486	C(202)	0.810(2)	0.2861(3)	0.1050(5)	0.0792
C(22)	0.4597(7)	0.3817(2)	0.7125(4)	0.0400	C(203)	0.704(2)	0.2625(3)	0.1191(6)	0.0752
C(23)	0.4800(8)	0.3608(2)	0.7731(4)	0.0468	C(204)	0.577(2)	0.2737(3)	0.1442(5)	0.0740
C(24)	0.3871(9)	0.3310(2)	0.7725(4)	0.0506	C(205)	0.560(1)	0.3096(2)	0.1561(4)	0.0562
C(25)	0.2798(8)	0.3226(2)	0.7129(4)	0.0456	N(210)	0.8365(6)	0.3835(2)	0.1228(3)	0.0478
C(26)	0.2674(7)	0.3449(2)	0.6547(4)	0.0374	C(211)	0.9194(9)	0.4121(3)	0.1138(4)	0.0627
C(27)	0.1590(8)	0.3418(2)	0.5836(4)	0.0458	C(212)	1.051(1)	0.4103(4)	0.0853(6)	0.0865
O(211)	0.5037(6)	0.4283(1)	0.6366(3)	0.0604	C(213)	1.097(1)	0.3782(6)	0.0647(7)	0.0882
O(212)	0.6416(6)	0.4276(2)	0.7462(3)	0.0679	C(214)	1.014(1)	0.3485(4)	0.0722(6)	0.0686
O(271)	0.1718(6)	0.3682(1)	0.5412(3)	0.0571	C(215)	0.884(1)	0.3513(3)	0.1031(4)	0.0597
O(272)	0.0740(6)	0.3166(1)	0.5720(3)	0.0622	N(250)	0.4648(6)	0.3636(2)	0.1974(3)	0.0468
N(31)	0.3251(7)	0.4447(2)	0.4917(3)	0.0497	C(251)	0.3671(9)	0.3835(2)	0.2282(4)	0.0601
C(31)	0.169(1)	0.4729(3)	0.5623(5)	0.0581	C(252)	0.245(1)	0.3672(4)	0.2523(6)	0.0765
C(32)	0.252(1)	0.4751(2)	0.4991(5)	0.0560	C(253)	0.223(1)	0.3311(4)	0.2433(7)	0.0817
C(33)	0.264(1)	0.5033(3)	0.4540(7)	0.0833	C(254)	0.321(1)	0.3116(3)	0.2102(6)	0.0764
C(34)	0.352(2)	0.4985(4)	0.4015(7)	0.0841	C(255)	0.443(1)	0.3276(2)	0.1874(4)	0.0523
C(35)	0.423(1)	0.4668(4)	0.3951(6)	0.0894					

[a] Equivalent isotropic *U*(iso) defined as one-third of the trace of the orthogonalized tensor.

$[Fe^{II}(tpy)_2][(dipic)_2Fe^{III}]_2$ crystallizes with one molecule of water and three molecules of acetonitrile. These latter molecules are probably disordered, as indicated by the high temperature factors of the carbon and nitrogen atoms. This disorder has not been solved. The geometry of these molecules was refined using slack constraints and isotropic temperature factors.

For $[Fe^{II}(tppz)_2][(dipic)_2Fe^{III}]_3$, due to the poor quality of the crystal, the number of reflections used for the refinements was rather small. Therefore, only the three iron atoms and the non-H atoms of the tppz ligands have been refined with their anisotropic temperature factors. The asymmetric unit contains disordered molecules of water. In a first step, the oxygen atom positions were refined with variable occupation factors and an isotropic temperature factor of 0.08 Å^2. After convergence, these occupation factors were fixed to the value closest to 1, $^2/_3$, $^1/_2$, or $^1/_3$ and the temperature factors were refined isotropically. A total of 12 water molecules were placed over 23 positions. Only 15 water hydrogen atoms were localized on difference Fourier maps. It was not possible to determine the H_3O^+ position.

Results and Discussion

$[(dipic)Fe^{III}(X)(OH_2)_2]$ Complexes (X = Cl, Br). These complexes are obtained from the binuclear $[(dipic)(H_2O)Fe^{III}(\mu\text{-}OH)_2Fe^{III}(OH_2)(dipic)]$ complex. The latter can be obtained by reaction of $dipicH_2$ and $FeCl_3$ in hot water (24 h, yield 60%).[5] We have devised a new synthesis by room-temperature oxidation of $[(dipic)Fe^{II}(OH_2)_3]$[1] giving a 92% yield. The product was obtained either by (slow) air oxidation of a stirred aqueous solution or by addition of bromine water according to (1).

$$2[(dipic)Fe^{II}(OH_2)_3] + Br_2 \rightarrow [(dipic)(H_2O)Fe^{III}(\mu\text{-}OH)]_2 + 2H_3O^+ + 2Br^- \quad (1)$$

Although two steps are necessary in starting from the iron salt, this method was found faster and more efficient than Potenza's method. When the reaction proceeds at higher concentration and with heating, the μ-hydroxo bridges are hydrolyzed by HBr generated in situ during the oxidation and one obtains the mononuclear complex $[(dipic)(Br)Fe^{III}(OH_2)_2]$ according to (2).

---

(5) Thich, J. A.; Ou, C. C.; Powers, D.; Wasiliou, B.; Mastropaolo, D.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1976**, *98*, 1425.

$$[(\mathrm{dipic})(\mathrm{H_2O})\mathrm{Fe^{III}}(\mu\text{-}\mathrm{OH})]_2 + 2\mathrm{H^+} + 2\mathrm{Br^-} \rightarrow 2[(\mathrm{dipic})(\mathrm{Br})\mathrm{Fe^{III}}(\mathrm{OH_2})_2] \quad (2)$$

This reaction can be extended to other acids and allows the synthesis of $[(\mathrm{dipic})(\mathrm{X})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ by reaction of HX and $[(\mathrm{dipic})(\mathrm{H_2O})\mathrm{Fe^{III}}(\mu\text{-}\mathrm{OH})]_2$.

Figure 1 shows the molecular unit of $[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ (**1**). Selected bond lengths and angles are given in Table 3. The molecule is located on a crystallographic 2-fold axis which goes through H(4), C(4), N(1), Fe(1), and Cl(1). This geometry is very close to that observed for $[(\mathrm{dipic})\mathrm{Fe^{II}}(\mathrm{OH_2})_3]$,[1] with the chloride ion replacing the water molecule *trans* to the dipic nitrogen atom. However, the larger chlorine van der Waals radius in addition to the smaller coordination sphere around $\mathrm{Fe^{III}}$ than around $\mathrm{Fe^{II}}$ induces more important steric repulsions between the chlorine atom and the axial water oxygen atoms in this complex than between the equatorial and the axial water oxygen atoms in $[(\mathrm{dipic})\mathrm{Fe^{II}}(\mathrm{OH_2})_3]$. As a consequence, the angles Cl(1)−Fe(1)−O(110) become obtuse at 94.24(6)° [88.66(6) and 84.38(6)° in $[(\mathrm{dipic})\mathrm{Fe^{II}}(\mathrm{OH_2})_3]$] and an inverse folding of O(110)−Fe(1)−O(110)′ is observed [171.5(1)°] [191.33(6)° in $[(\mathrm{dipic})\mathrm{Fe^{II}}(\mathrm{OH_2})_3]$]. In the crystal, the intermolecular hydrogen bonds are weak with O(11)−H(117) = 1.94(5) Å, O(11)−O(110) = 2.70(3) Å and O(12)−H(116) = 1.98(5) Å, O(12)−O(110) = 2.729(3) Å. Measurement of the cell parameters of the bromine derivatives and comparison of diffraction patterns show that it is isostructural with the chlorine derivative.

The $[(\mathrm{dipic})(\mathrm{X})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ complexes are not stable in aqueous solution at pH >1 and give back the dinuclear μ-hydroxo complex. They are stable in methanol, which allows spectrophotometric and electrochemical studies.

The voltammogram of the chlorine derivative in MeOH/$\mathrm{TBAPF_6}$ showed one irreversible wave at −55 mV vs SCE corresponding to the one-electron reduction $\mathrm{Fe^{III}/Fe^{II}}$. For the bromine derivative, the voltammogram shows two waves: an irreversible one at +250 mV and a quasi-reversible one at +82 mV vs SCE, corresponding to two species in solution. Comparison of the UV−visible spectra of methanolic solutions of this compound at various concentrations shows that the optical density of the bromine to iron(III) charge transfer band at 371.5 nm decreases with increasing dilution. Furthermore, addition of tetrabutylammonium bromide to a solution of the product increases this optical density up to a plateau $\epsilon = 2930$ L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$. This indicates that $[(\mathrm{dipic})(\mathrm{Br})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ is in equilibrium with the solvent S, according to (3).

$$[(\mathrm{dipic})(\mathrm{Br})\mathrm{Fe^{III}}(\mathrm{OH_2})_2] + \mathrm{S} \rightleftarrows [(\mathrm{dipic})\mathrm{Fe^{III}}(\mathrm{S})(\mathrm{OH_2})_2]^+ + \mathrm{Br^-} \quad (3)$$

Thus we assign the 82 mV wave to the reduction of $[(\mathrm{dipic})(\mathrm{Br})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ and the 250 mV wave to the reduction of $[(\mathrm{dipic})\mathrm{Fe^{III}}(\mathrm{S})(\mathrm{OH_2})_2]^+$, assuming that the uncharged species is oxidized first.

The chloride complex is more stable in solution. This is a general tendency for chloride vs bromide complexes of iron(III) and can be related to the harder basic character of $\mathrm{Cl^-}$ compared with $\mathrm{Br^-}$. Thus, $\mathrm{Cl^-}$ has a better affinity for the hard acid $\mathrm{Fe^{III}}$, using HSAB terminology.[6]

Finally, a magnetic susceptibility study of $[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ and $[(\mathrm{dipic})(\mathrm{Br})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ showed constant magnetic moments (i.e. Curie's law is followed) between 300 K (μ = 5.92 and 5.96 μ_B respectively) and 120 K. Below 120 K, the magnetic moments dropped rapidly down to 3.55 and 3.17 μ_B at 4.35 K. This decrease is too large to be attributed to zero-field splitting. Furthermore, the lack of strong intermolecular hydrogen bonds and the long Fe−Fe distances (minimum 5.018 Å) preclude any significant intermolecular interaction. This result remains unexplained.

Table 9. Selected Bond Distances (Å) and Angles (deg) for $[\mathrm{Fe^{II}}(\mathrm{tpy})_2][(\mathrm{dipic})_2\mathrm{Fe^{III}}]_2\cdot\mathrm{H_2O}\cdot3\mathrm{CH_3CN}$ (**4**)

Fe(1)−N(1)	2.062(5)	C(1)−O(12)	1.221(9)
Fe(1)−O(11)	2.004(5)	C(7)−O(71)	1.300(9)
Fe(1)−O(71)	2.065(6)	C(7)−O(72)	1.227(9)
Fe(1)−N(11)	2.054(6)	C(11)−O(111)	1.281(8)
Fe(1)−O(111)	2.032(5)	C(11)−O(112)	1.215(8)
Fe(1)−O(171)	1.992(5)	C(17)−O(171)	1.294(9)
C(1)−O(11)	1.281(9)	C(17)−O(172)	1.201(8)
Fe(2)−N(21)	2.046(5)	C(21)−O(212)	1.221(8)
Fe(2)−O(211)	2.031(5)	C(27)−O(271)	1.290(9)
Fe(2)−O(271)	1.995(5)	C(27)−O(272)	1.205(9)
Fe(2)−N(31)	2.044(6)	C(31)−O(311)	1.28(1)
Fe(2)−O(311)	2.015(6)	C(31)−O(312)	1.21(1)
Fe(2)−O(371)	1.999(6)	C(37)−O(371)	1.27(1)
C(21)−O(211)	1.288(8)	C(37)−O(372)	1.22(1)
Fe(3)−N(100)	1.875(5)	Fe(3)−N(200)	1.881(6)
Fe(3)−N(110)	1.968(5)	Fe(3)−N(210)	1.980(6)
Fe(3)−N(150)	1.982(5)	Fe(3)−N(250)	1.975(6)

O(11)−Fe(1)−N(1)	76.4(2)	O(111)−Fe(1)−O(71)	94.1(2)
O(71)−Fe(1)−N(1)	75.0(2)	O(111)−Fe(1)−N(11)	75.4(2)
O(71)−Fe(1)−O(11)	151.3(2)	O(171)−Fe(1)−N(1)	109.3(2)
N(11)−Fe(1)−N(1)	162.4(2)	O(171)−Fe(1)−O(11)	94.7(2)
N(11)−Fe(1)−O(11)	120.5(2)	O(171)−Fe(1)−O(71)	92.7(2)
N(11)−Fe(1)−O(71)	88.2(2)	O(171)−Fe(1)−N(11)	76.0(2)
O(111)−Fe(1)−N(1)	100.2(2)	O(171)−Fe(1)−O(111)	150.4(2)
O(111)−Fe(1)−O(11)	93.0(2)		
O(211)−Fe(2)−N(21)	75.7(2)	O(311)−Fe(2)−O(271)	94.0(2)
O(271)−Fe(2)−N(21)	76.3(2)	O(311)−Fe(2)−N(31)	76.1(3)
O(271)−Fe(2)−O(211)	152.0(2)	O(371)−Fe(2)−N(21)	107.1(2)
N(31)−Fe(2)−N(21)	169.9(2)	O(371)−Fe(2)−O(211)	96.5(2)
N(31)−Fe(2)−O(211)	94.5(2)	O(371)−Fe(2)−O(271)	90.9(2)
N(31)−Fe(2)−O(271)	113.5(2)	O(371)−Fe(2)−N(31)	75.8(3)
O(311)−Fe(2)−N(21)	101.7(2)	O(371)−Fe(2)−O(311)	151.1(2)
O(311)−Fe(2)−O(211)	92.4(2)		
N(110)−Fe(3)−N(100)	81.7(2)	N(210)−Fe(3)−N(150)	92.3(2)
N(150)−Fe(3)−N(100)	81.1(2)	N(210)−Fe(3)−N(200)	81.3(3)
N(150)−Fe(3)−N(110)	162.8(2)	N(250)−Fe(3)−N(100)	99.9(2)
N(200)−Fe(3)−N(100)	179.4(3)	N(250)−Fe(3)−N(110)	91.6(2)
N(200)−Fe(3)−N(110)	98.7(2)	N(250)−Fe(3)−N(150)	91.6(2)
N(200)−Fe(3)−N(150)	98.5(2)	N(250)−Fe(3)−N(200)	80.5(3)
N(210)−Fe(3)−N(100)	98.3(3)	N(250)−Fe(3)−N(210)	161.8(3)
N(210)−Fe(3)−N(110)	90.0(2)		

[(dipic)(acac)$\mathrm{Fe^{III}}$S] (2) (S = Solvent). As a consequence of our interest in precursors and building blocks with only one avalaible coordination site, we prepared several derivatives of the type $[(\mathrm{dipic})\mathrm{Fe^{III}}\mathrm{L}(\mathrm{AA})]^+$ where L is a labile unidentate ligand, while AA is a chelating ligand assumed to be more difficult to displace. Mononuclear coordination compounds of iron(III) or iron(IV) showing a "$\mathrm{NO_5}$" environment are also of potential interest in catalysis.[7] Examples are $[(\mathrm{dipic})(\mathrm{acac})\mathrm{Fe^{III}S}]$ (S = solvent) and $[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{phen})]$.

---

(6) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.

(7) (a) Sheu, C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 8212. (b) Sugimoto, H.; Tung, H.-C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 2465. (c) Dalton, H. *Adv. Appl. Microbiol.* **1980**, *26*, 71. (d) Ericson, A.; Hedman, B.; Hodgson, K. O.; Green, J. ; Dalton, H.; Bentsen, J. G.; Beer, S.; Lippard, S. J. *J. Am. Chem Soc.* **1988**, *110*, 2330. (e) Fox, B. G.; Surerus, K. K.; Munck, E.; Lipscomb, J. D. *J. Biol. Chem.* **1988**, *263*, 10553. (f) Sheu, C.; Sobkowiak, A.; Jeon, S.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 879. (g) Cofré, P.; Richert, S. A.; Sobkowiak, A.; Sawyer, D. T. *Inorg. Chem.* **1990**, *29*, 2645. (h) Tung, H.-C.; Kang, C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1992**, *114*, 3445. (i) Balavoine, G; Barton, D. H. R.; Gref, A.; Lellouche, I. *Tetrahedron* **1992**, *48*, 1883.

Table 10. Selected Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_3$·H$_3$O·11H$_2$O (**5**)

atom	*x/a*	*y/b*	*z/c*	*U*(iso)	atom	*x/a*	*y/b*	*z/c*	*U*(iso)
Fe(1)	0.4937(1)	0.2271(1)	0.9801(1)	0.0694	C(55)	0.2945(7)	0.2080(7)	0.8004(8)	0.059(5)
N(1)	0.4851(6)	0.2340(5)	0.9006(6)	0.061(4)	C(56)	0.2853(6)	0.2194(6)	0.7468(7)	0.047(4)
C(1)	0.5481(7)	0.2919(6)	0.9546(8)	0.055(5)	C(57)	0.2497(7)	0.1965(6)	0.6864(8)	0.055(5)
C(2)	0.5119(7)	0.2663(6)	0.8968(8)	0.053(5)	O(511)	0.3449(5)	0.3189(5)	0.7147(6)	0.073(4)
C(3)	0.5050(8)	0.2756(7)	0.8432(9)	0.073(6)	O(512)	0.3949(5)	0.3471(5)	0.8074(6)	0.086(4)
C(4)	0.4700(9)	0.2452(8)	0.796(1)	0.086(7)	O(571)	0.2483(4)	0.2139(4)	0.6429(5)	0.063(3)
C(5)	0.4435(8)	0.2111(7)	0.8004(9)	0.072(6)	O(572)	0.2221(5)	0.1632(4)	0.6808(5)	0.068(4)
C(6)	0.4516(7)	0.2049(7)	0.8547(9)	0.067(6)	Fe(4)	0.7216(1)	0.49918(8)	1.0138(1)	0.0386
C(7)	0.4267(9)	0.1728(8)	0.874(1)	0.085(7)	N(100)	0.7570(5)	0.4983(5)	0.9797(6)	0.0363
O(11)	0.5453(5)	0.2766(5)	0.9970(6)	0.069(4)	C(101)	0.7982(7)	0.5234(6)	1.0026(8)	0.0475
O(12)	0.5744(5)	0.3239(5)	0.9589(6)	0.080(4)	C(102)	0.8264(6)	0.5197(6)	0.9796(8)	0.0439
O(71)	0.4396(5)	0.1785(5)	0.9264(7)	0.088(4)	N(103)	0.8086(5)	0.4965(5)	0.9303(6)	0.0443
O(72)	0.3952(6)	0.1433(6)	0.8365(7)	0.106(5)	C(104)	0.7643(7)	0.4729(6)	0.9032(7)	0.0463
N(11)	0.5043(6)	0.2260(5)	1.0619(6)	0.059(4)	C(105)	0.7386(6)	0.4697(6)	0.9301(7)	0.0363
C(11)	0.4411(7)	0.2856(7)	1.0132(9)	0.063(5)	N(110)	0.7709(5)	0.5487(5)	1.0623(6)	0.0449
C(12)	0.4787(7)	0.2579(7)	1.0708(8)	0.065(5)	C(111)	0.7739(7)	0.5757(6)	1.1042(8)	0.0473
C(13)	0.4883(7)	0.2600(7)	1.1262(9)	0.065(5)	C(112)	0.8111(7)	0.6077(7)	1.1398(9)	0.0544
C(14)	0.5245(7)	0.2305(7)	1.1711(9)	0.069(6)	C(113)	0.8466(9)	0.6139(6)	1.1297(8)	0.0526
C(15)	0.5488(7)	0.1981(7)	1.1608(8)	0.064(5)	C(114)	0.8446(7)	0.5892(7)	1.0848(9)	0.0625
C(16)	0.5383(8)	0.1951(7)	1.1043(9)	0.068(6)	C(115)	0.8064(7)	0.5545(6)	1.0520(7)	0.0432
C(17)	0.5610(8)	0.1663(7)	1.0794(9)	0.067(6)	N(120)	0.9145(7)	0.5271(6)	1.0629(9)	0.0651
O(111)	0.4450(5)	0.2760(5)	0.9708(6)	0.075(4)	C(121)	0.9611(9)	0.545(1)	1.089(1)	0.1025
O(112)	0.4130(5)	0.3139(5)	1.0119(6)	0.082(4)	C(122)	0.969(1)	0.577(1)	1.058(2)	0.1184
O(171)	0.5466(5)	0.1761(5)	1.0270(6)	0.083(4)	C(123)	0.934(1)	0.593(1)	1.004(2)	0.1123
O(172)	0.5920(6)	0.1343(5)	1.1124(6)	0.088(4)	C(124)	0.888(1)	0.574(1)	0.978(1)	0.0802
Fe(2)	0.1691(1)	0.2218(1)	0.8173(1)	0.0565	C(125)	0.8778(8)	0.5421(7)	1.006(1)	0.0606
N(21)	0.1581(5)	0.2340(5)	0.7368(6)	0.049(4)	N(140)	0.6974(6)	0.4611(5)	0.7978(7)	0.0498
C(21)	0.2183(7)	0.2943(7)	0.7940(8)	0.057(5)	C(141)	0.6825(8)	0.4438(8)	0.7442(9)	0.0630
C(22)	0.1828(6)	0.2694(6)	0.7339(7)	0.047(4)	C(142)	0.713(1)	0.4169(7)	0.7349(9)	0.0572
C(23)	0.1752(7)	0.2792(7)	0.6791(8)	0.061(5)	C(143)	0.761(1)	0.4087(7)	0.782(1)	0.0591
C(24)	0.1435(7)	0.2499(7)	0.6323(8)	0.061(5)	C(144)	0.7776(7)	0.4258(6)	0.8380(8)	0.0540
C(25)	0.1185(7)	0.2139(7)	0.6360(8)	0.065(5)	C(145)	0.7456(7)	0.4514(6)	0.8444(8)	0.0391
C(26)	0.1258(7)	0.2063(6)	0.6906(8)	0.056(5)	N(150)	0.6821(5)	0.4489(5)	0.9546(6)	0.0413
C(27)	0.1026(8)	0.1711(7)	0.707(1)	0.072(6)	C(151)	0.6430(6)	0.4248(6)	0.9464(7)	0.0395
O(211)	0.2161(4)	0.2760(4)	0.8357(5)	0.057(3)	C(152)	0.6160(6)	0.3917(6)	0.9020(8)	0.0437
O(212)	0.2444(5)	0.3269(5)	0.8001(6)	0.072(4)	C(153)	0.6302(7)	0.3825(6)	0.8647(8)	0.0432
O(271)	0.1162(5)	0.1734(5)	0.7612(6)	0.073(4)	C(154)	0.6707(7)	0.4069(6)	0.8727(8)	0.0462
O(272)	0.0707(6)	0.1415(6)	0.6693(7)	0.094(5)	C(155)	0.6956(6)	0.4411(5)	0.9164(7)	0.0341
N(31)	0.1827(5)	0.2142(5)	0.8994(6)	0.051(4)	N(200)	0.6873(5)	0.5004(5)	1.0500(6)	0.0335
C(31)	0.1162(8)	0.2673(8)	0.8588(9)	0.076(6)	C(201)	0.7078(6)	0.4737(6)	1.1009(7)	0.0382
C(32)	0.1547(7)	0.2401(7)	0.9116(9)	0.066(6)	C(202)	0.6842(7)	0.4801(5)	1.1307(7)	0.0368
C(33)	0.1667(9)	0.2350(8)	0.968(1)	0.086(7)	N(203)	0.6407(5)	0.5031(5)	1.1048(6)	0.0405
C(34)	0.2034(8)	0.2068(8)	1.0083(9)	0.075(6)	C(204)	0.6203(7)	0.5248(6)	1.0523(9)	0.0434
C(35)	0.2314(8)	0.1798(7)	0.9968(9)	0.073(6)	C(205)	0.6462(6)	0.5271(6)	1.0259(7)	0.0339
C(36)	0.2195(7)	0.1858(7)	0.9378(8)	0.059(5)	N(210)	0.7638(5)	0.4534(4)	1.0772(6)	0.0324
C(37)	0.2430(9)	0.1625(8)	0.912(1)	0.081(6)	C(211)	0.8038(8)	0.4307(6)	1.0874(8)	0.0519
O(311)	0.1175(5)	0.2641(4)	0.8129(6)	0.072(4)	C(212)	0.8307(7)	0.3973(7)	1.1324(9)	0.0492
O(312)	0.0854(6)	0.2933(5)	0.8586(7)	0.095(5)	C(213)	0.8178(7)	0.3886(7)	1.1711(9)	0.0566
O(371)	0.2251(5)	0.1741(4)	0.8584(6)	0.069(4)	C(214)	0.7773(7)	0.4122(6)	1.1621(8)	0.0504
O(372)	0.2770(6)	0.1309(6)	0.9410(7)	0.111(5)	C(215)	0.7521(6)	0.4453(5)	1.1171(7)	0.0310
Fe(3)	0.2948(1)	0.2683(1)	0.6595(1)	0.0565	N(220)	0.7528(6)	0.4694(5)	1.2344(7)	0.0522
N(41)	0.2964(5)	0.2815(5)	0.5868(6)	0.056(4)	C(221)	0.7713(7)	0.4526(8)	1.2896(8)	0.0609
C(41)	0.3619(9)	0.2279(8)	0.637(1)	0.086(7)	C(222)	0.7441(9)	0.4271(7)	1.3023(9)	0.0620
C(42)	0.3314(7)	0.2596(6)	0.5856(8)	0.057(5)	C(223)	0.6939(9)	0.4181(7)	1.257(1)	0.0607
C(43)	0.3365(8)	0.2698(8)	0.539(1)	0.083(6)	C(224)	0.6740(7)	0.4344(6)	1.2002(8)	0.0485
C(44)	0.3033(9)	0.3008(8)	0.499(1)	0.085(7)	C(225)	0.7049(7)	0.4589(6)	1.1908(8)	0.0467
C(45)	0.2673(8)	0.3231(8)	0.498(1)	0.084(7)	N(240)	0.5651(7)	0.5796(7)	1.0615(9)	0.0920
C(46)	0.2635(8)	0.3140(7)	0.5457(9)	0.073(6)	C(241)	0.514(1)	0.5979(9)	1.033(1)	0.0701
C(47)	0.2313(9)	0.3302(9)	0.561(1)	0.096(8)	C(242)	0.4741(9)	0.584(1)	0.978(1)	0.0742
O(411)	0.3500(5)	0.2242(5)	0.6727(6)	0.072(4)	C(243)	0.486(1)	0.552(1)	0.951(1)	0.0880
O(412)	0.3986(7)	0.2045(6)	0.6438(7)	0.112(6)	C(244)	0.5307(6)	0.5334(6)	0.9732(7)	0.0217
O(471)	0.2375(5)	0.3135(5)	0.6095(6)	0.083(4)	C(245)	0.5693(7)	0.5475(7)	1.0263(9)	0.0486
O(472)	0.1989(7)	0.3617(7)	0.5298(8)	0.128(6)	N(250)	0.6685(5)	0.5454(5)	0.9605(6)	0.0417
N(51)	0.3078(5)	0.2562(5)	0.7404(6)	0.045(4)	C(251)	0.6628(7)	0.5676(6)	0.9151(8)	0.0457
C(51)	0.3621(8)	0.3199(7)	0.7695(9)	0.067(6)	C(252)	0.6254(8)	0.6000(7)	0.8818(9)	0.0493
C(52)	0.3416(7)	0.2826(6)	0.7873(8)	0.055(5)	C(253)	0.5922(7)	0.6125(7)	0.8952(8)	0.0554
C(53)	0.3518(7)	0.2748(7)	0.8430(8)	0.062(5)	C(254)	0.5973(7)	0.5889(7)	0.9425(9)	0.0538
C(54)	0.3266(8)	0.2363(7)	0.8468(9)	0.071(6)	C(255)	0.6343(7)	0.5547(6)	0.9745(7)	0.0399

[a] Equivalent isotropic *U*(iso) defined as one-third of the trace of the orthogonalized tensor.

[(dipic)(acac)Fe^{III}S] can be prepared by reaction of dipicH$_2$ and [(acac)$_3$Fe^{III}] in ethanol according to Hoof and Walton[3a] and to Aly and El-Awad.[3b] These authors proposed two formulations: [(dipic)(acac)Fe^{III}(OH$_2$)] and [(dipic)Fe^{III}(acac)]$_n$, the latter being coordinatively unsaturated and thus probably polymeric. The experimental evidence was however dubious.

We have also prepared this compound by reaction of the μ-hydroxo dimer with acetylacetone in very good yield (94%) according to (4).

$$[(\mathrm{dipic})(\mathrm{H_2O})\mathrm{Fe^{III}}(\mu\text{-}\mathrm{OH})]_2 + 2\mathrm{acacH} \rightarrow 2[(\mathrm{dipic})(\mathrm{acac})\mathrm{Fe^{III}}(\mathrm{OH_2})] + 2\mathrm{H_2O} \quad (4)$$

Finally, it can be prepared by reaction of acetylacetone with the chlorinated monomer (yield 89%) according to (5).

$$[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{OH_2})_2] + \mathrm{acacH} \rightarrow [(\mathrm{dipic})(\mathrm{acac})\mathrm{Fe^{III}}(\mathrm{OH_2})] + \mathrm{H_3O^+} + \mathrm{Cl^-} \quad (5)$$

Microanalysis is in agreement with the above formulation, and the crystal structure described below shows that the water molecule is indeed coordinated to iron. We have not been able to reproduce the work of Aly et al., who described an anhydrous form $[(\mathrm{dipic})\mathrm{Fe^{III}}(\mathrm{acac})]$.

The crystal structure was solved using a batch prepared by method a.[3] The molecular structure of $[(\mathrm{dipic})(\mathrm{acac})\mathrm{Fe^{III}}(\mathrm{OH_2})]$ (**2**) is shown on Figure 2, and selected bond lengths and angles are presented in Table 5. The asymmetric unit contains also half a molecule of ethanol disordered around the binary axis (this "half-molecule" is not detected by microanalysis). To the distorted octahedral iron(III) center are bound a molecule of water, one $\mathrm{acac^-}$ ligand, and one $\mathrm{dipic^{2-}}$ ligand. The two latter ligands are planar (maximum deviation 0.085 Å) with a dihedral angle between their mean planes of 104.6°. The Fe−O distances are normal for an $\mathrm{Fe^{III}}$ complex: 2.035(2) and 2.046(2) Å for $\mathrm{dipic^{2-}}$ and 1.935(2) and 1.977(2) Å for $\mathrm{acac^-}$.

Thus $[(\mathrm{dipic})(\mathrm{acac})\mathrm{Fe^{III}}(\mathrm{OH_2})]$ is actually molecular and not polymeric as assumed elsewhere.[3a] It should be noted that the hypothesis of a polymeric structure $[(\mathrm{dipic})(\mathrm{acac})\mathrm{Fe^{III}}]_n{\cdot}n\mathrm{H_2O}$ relied only on IR spectroscopy and was not particularly convincing.

$[(\mathrm{dipic})(\mathrm{X})\mathrm{Fe^{III}}(\mathrm{phen})]$ Complexes (X = Cl, Br). $[(\mathrm{dipic})(\mathrm{X})\mathrm{Fe^{III}}(\mathrm{phen})]$ (X = Br or Cl) can be prepared by reaction of $[(\mathrm{dipic})(\mathrm{X})\mathrm{Fe^{III}}(\mathrm{OH_2})_2]$ and 1,10-phenanthroline (yields 88−90%). The X-ray structure of the chloride derivative (**3**) has been solved (see Figure 3). The molecule crystallizes in space group $P2_1/n$ with one dichloromethane molecule (recrystallization solvent) per asymmetric unit. Selected bond lengths and angles are grouped in Table 7. The dihedral angle between the mean planes defined by the two aromatic ligands is 93.8°. The chlorine atom Cl(1) is in the phenanthroline mean plane. Steric repulsion between this chlorine atom and N(1), O(11), and O(71) is released by an increase of the angle N(1)−Fe(1)−Cl(1) (101.75°).

The iron−phenanthroline distances [2.149(2) and 2.186(2) Å] are in the same range as in $[\mathrm{Fe^{III}}(\mathrm{phen})(\mathrm{OH_2})_3]^{3+}$,[8] and the Fe−Cl distances are close to those found in $[(\mathrm{Cl})_3\mathrm{Fe^{III}}(\mathrm{phen})(\mathrm{OH_2})]$[9] and $[(\mathrm{Cl})_3\mathrm{Fe^{III}}(\mathrm{phen})(\mathrm{dmf})]$.[10]

The magnetic susceptibility of $[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{phen})]$ follows Curie's law down to 20 K. At 300 K, $\mu = 6.13\ \mu_\mathrm{B}$, which indicates that the iron atom is an isolated high-spin Fe(III). Below 20 K, its value decreases steadily down to 5.66 μ_B at 4.3 K. As there is no hydrogen bonding in the crystal, these experimental results can be simulated by zero-field splitting with $g = 2.07$, $|D| = 2.07\ \mathrm{cm^{-1}}$ (residual = 0.16×10^{-4}).

Table 11. Selected Bond Distances (Å) and Angles (deg) for $[\mathrm{Fe^{II}}(\mathrm{tppz})_2][(\mathrm{dipic})_2\mathrm{Fe^{III}}]_3{\cdot}\mathrm{H_3O}{\cdot}11\mathrm{H_2O}$ (**5**)

Fe(1)−N(1)	2.05(1)	C(1)−O(12)	1.20(2)
Fe(1)−O(11)	2.01(1)	C(7)−O(71)	1.26(2)
Fe(1)−O(71)	2.02(1)	C(7)−O(72)	1.25(2)
Fe(1)−N(11)	2.07(1)	C(11)−O(111)	1.28(2)
Fe(1)−O(111)	2.00(1)	C(11)−O(112)	1.20(2)
Fe(1)−O(171)	2.02(1)	C(17)−O(171)	1.26(2)
C(1)−O(11)	1.30(2)	C(17)−O(172)	1.25(2)
Fe(2)−N(21)	2.06(1)	C(21)−O(212)	1.20(2)
Fe(2)−O(211)	2.00(1)	C(27)−O(271)	1.29(2)
Fe(2)−O(271)	2.02(1)	C(27)−O(272)	1.26(2)
Fe(2)−N(31)	2.05(1)	C(31)−O(311)	1.30(2)
Fe(2)−O(311)	2.00(1)	C(31)−O(312)	1.24(2)
Fe(2)−O(371)	1.99(1)	C(37)−O(371)	1.28(2)
C(21)−O(211)	1.30(2)	C(37)−O(372)	1.27(2)
Fe(3)−N(41)	2.07(1)	C(41)−O(412)	1.27(2)
Fe(3)−O(411)	2.03(1)	C(47)−O(471)	1.31(2)
Fe(3)−O(471)	1.99(1)	C(47)−O(472)	1.25(3)
Fe(3)−N(51)	2.04(1)	C(51)−O(511)	1.27(2)
Fe(3)−O(511)	2.02(1)	C(51)−O(512)	1.23(2)
Fe(3)−O(571)	2.01(1)	C(57)−O(571)	1.27(2)
C(41)−O(411)	1.27(2)	C(57)−O(572)	1.25(2)
Fe(4)−N(100)	1.87(1)	Fe(4)−N(200)	1.89(1)
Fe(4)−N(110)	1.94(1)	Fe(4)−N(210)	1.94(1)
Fe(4)−N(150)	1.96(1)	Fe(4)−N(250)	1.96(1)
O(11)−Fe(1)−N(1)	75.4(6)	O(111)−Fe(1)−O(71)	95.7(6)
O(71)−Fe(1)−N(1)	76.8(6)	O(111)−Fe(1)−N(11)	76.0(6)
O(71)−Fe(1)−O(11)	152.2(6)	O(171)−Fe(1)−N(1)	106.2(6)
N(11)−Fe(1)−N(1)	175.2(6)	O(171)−Fe(1)−O(11)	94.3(5)
N(11)−Fe(1)−O(11)	100.4(5)	O(171)−Fe(1)−O(71)	91.3(6)
N(11)−Fe(1)−O(71)	107.4(6)	O(171)−Fe(1)−N(11)	76.3(6)
O(111)−Fe(1)−N(1)	101.6(6)	O(171)−Fe(1)−O(111)	152.2(6)
O(111)−Fe(1)−O(11)	91.9(5)		
O(211)−Fe(2)−N(21)	76.5(5)	O(311)−Fe(2)−O(271)	93.4(5)
O(271)−Fe(2)−N(21)	76.2(5)	O(311)−Fe(2)−N(31)	75.8(5)
O(271)−Fe(2)−O(211)	152.6(5)	O(371)−Fe(2)−N(21)	104.2(5)
N(31)−Fe(2)−N(21)	176.1(6)	O(371)−Fe(2)−O(211)	94.3(5)
N(31)−Fe(2)−O(211)	99.7(5)	O(371)−Fe(2)−O(271)	92.9(5)
N(31)−Fe(2)−O(271)	107.7(5)	O(371)−Fe(2)−N(31)	76.8(5)
O(311)−Fe(2)−N(21)	103.3(5)	O(371)−Fe(2)−O(311)	152.5(5)
O(311)−Fe(2)−O(211)	92.4(5)		
O(411)−Fe(3)−N(41)	76.1(6)	O(511)−Fe(3)−O(471)	94.1(5)
O(471)−Fe(3)−N(41)	76.2(6)	O(511)−Fe(3)−N(51)	75.1(5)
O(471)−Fe(3)−O(411)	151.8(6)	O(571)−Fe(3)−N(41)	111.3(5)
N(51)−Fe(3)−N(41)	169.2(6)	O(571)−Fe(3)−O(411)	91.9(5)
N(51)−Fe(3)−O(411)	96.4(5)	O(571)−Fe(3)−O(471)	93.9(5)
N(51)−Fe(3)−O(471)	111.8(6)	O(571)−Fe(3)−N(51)	76.2(5)
O(511)−Fe(3)−N(41)	97.5(5)	O(571)−Fe(3)−O(511)	151.2(5)
O(511)−Fe(3)−O(411)	94.0(5)		
N(110)−Fe(4)−N(100)	81.7(6)	N(210)−Fe(4)−N(150)	91.7(5)
N(150)−Fe(4)−N(100)	82.2(6)	N(210)−Fe(4)−N(200)	81.8(6)
N(150)−Fe(4)−N(110)	163.8(6)	N(250)−Fe(4)−N(100)	99.2(6)
N(200)−Fe(4)−N(100)	178.7(6)	N(250)−Fe(4)−N(110)	92.0(6)
N(200)−Fe(4)−N(110)	97.2(6)	N(250)−Fe(4)−N(150)	90.5(6)
N(200)−Fe(4)−N(150)	98.9(6)	N(250)−Fe(4)−N(200)	81.5(6)
N(210)−Fe(4)−N(100)	97.4(6)	N(250)−Fe(4)−N(210)	163.4(6)
N(210)−Fe(4)−N(110)	90.5(5)		

The chemical stability of $[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{phen})]$ and $[(\mathrm{dipic})(\mathrm{acac})\mathrm{Fe^{III}}(\mathrm{OH_2})]$ is very high, and all attempts to substitute Cl or $\mathrm{H_2O}$ were unsuccessful. However prolonged heating of $[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{phen})]$ led to new mixed-valence compounds in which the inert $[(\mathrm{dipic})_2\mathrm{Fe^{III}}]^-$ is the counterion.

Structures with $[(\mathrm{dipic})_2\mathrm{Fe^{III}}]^-$ as Counterion. Thermal degradation of $[(\mathrm{dipic})(\mathrm{Cl})\mathrm{Fe^{III}}(\mathrm{phen})]$ in boiling acetonitrile for 48 h yields a purplish-red compound $[\mathrm{Fe^{II}}(\mathrm{phen})_3][(\mathrm{dipic})_2\mathrm{Fe^{III}}]_2{\cdot}3\mathrm{H_2O}$. We also prepared this product by reaction of $[(\mathrm{dipic})\mathrm{Fe^{II}}(\mathrm{OH_2})_3]$ with 1,10-phenanthroline (in air). There is thus a strong tendency for ligand redistribution which seems linked to the redox process: 1,10-phenanthroline, a good

---

[8] Healy, P. C.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 1405.

[9] Healy, P. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 2031.

[10] Reiff, W. M.; Witten, E. H.; Mottle, K.; Brennan, T. F.; Garafalo, A. R. *Inorg. Chim. Acta* **1983**, *77*, 227.

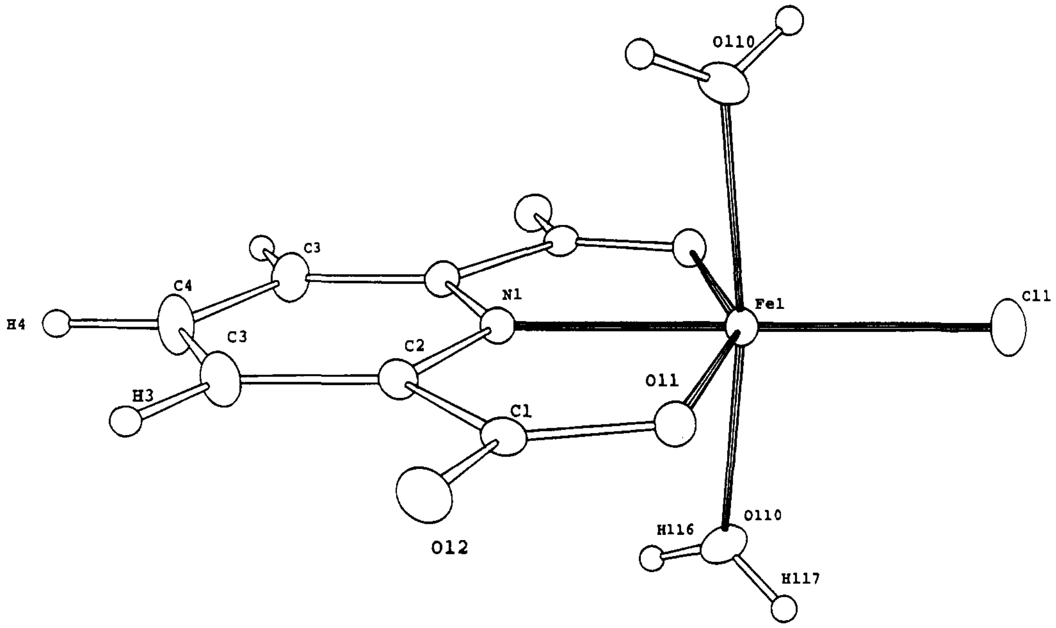

Figure 1. Molecular structure of the complex [(dipic)(Cl)$Fe^{III}(OH_2)_2$], **1**.

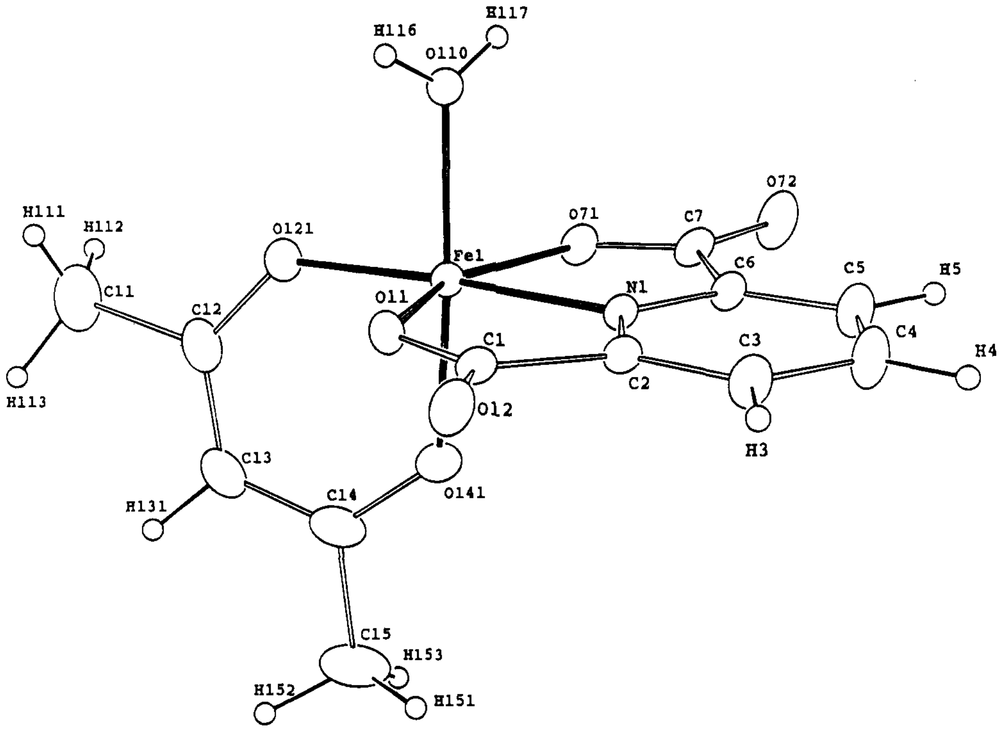

Figure 2. ORTEP diagram for [(dipic)(acac)$Fe^{III}(OH_2)$], **2**.

π-acceptor, stabilizes iron(II), while dipicolinate stabilizes iron(III). Consequently, there is a "sorting" of the ligands. The reducing agent responsible for the appearance of iron(II) has not been identified. Since the redox potential of the $[Fe(phen)_3]^{2+/3+}$ couple is very high, any mild reductant (solvent, impurities, excess ligand, ...) can generate iron(II) under these conditions.

Twinning of the crystals prevented a single-crystal X-ray determination. This mixed-valence formulation is compatible with magnetic data. Magnetic susceptibility measurements show a constant effective magnetic moment between 15 and 300 K. At 300 K, $\mu_{eff} = 8.645$ μ_B, which is consistent with one low-spin Fe^{II} in $[Fe^{II}(phen)_3]^{2+}$ and two high-spin Fe^{III} in $[(dipic)_2Fe^{III}]^-$; the effective moment decreases slightly between 15 and 4.3 K, where $\mu_{eff} = 8.33$ μ_B. These experimental results can be simulated by zero-field splitting with $g = 2.06$ and $|D| = 1.49$ cm^{-1} (residual 2.4×10^{-5}).

A similar reaction can be observed with 2,2′:6′,2″-terpyridine (tpy) and affords $[Fe^{II}(tpy)_2][(dipic)_2Fe^{III}]_2$ (**4**). The X-ray structure of the compound revealed that the asymmetric unit contains an iron(II) complex $[Fe^{II}(tpy)_2]^{2+}$, two iron(III) complexes $[(dipic)_2Fe^{III}]^-$, one molecule of water, and three molecules of acetonitrile, which was the recrystallization solvent. These complexes with atom-labeling schemes are shown in Figures 4 and 5. Selected bond lengths and angles are given in Table 9. In $[Fe^{II}(tpy)_2]^{2+}$, the two ligands are planar within 0.1 Å and perpendicular (angle between the mean planes 88.3°). The geometry is very close to that observed in $[Fe^{II}(tpy)_2](ClO_4)_2{\cdot}2H_2O$.[11] In particular, the bond lengths between the metal atom and the nitrogen atom of the central pyridine groups

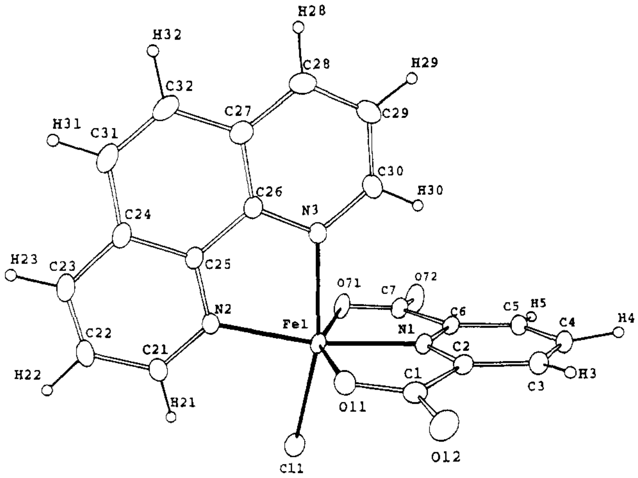

Figure 3. ORTEP drawing of the complex [(dipic)(Cl)Fe^{III}(phen)], **3**.

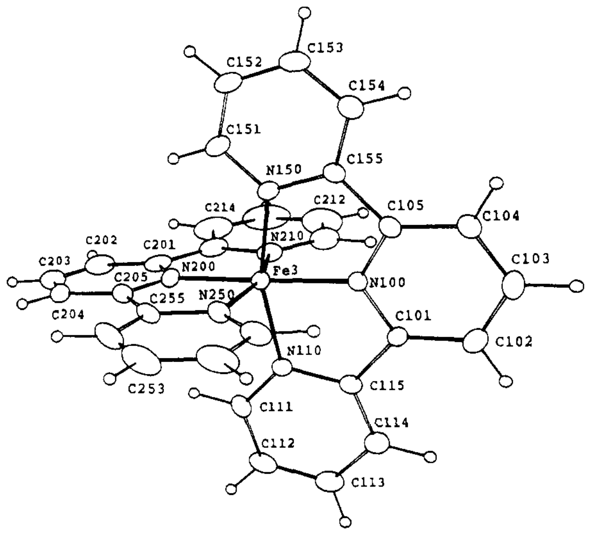

Figure 4. Structure of the cation [Fe^{II}(tpy)$_2$]$^{2+}$ in **4**.

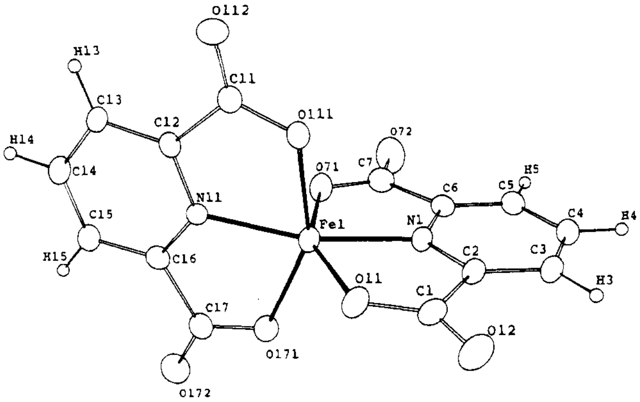

Figure 5. Structure of one of the anions [(dipic)$_2$Fe^{III}]$^-$ in **4**.

[1.875(5) and 1.881(6) Å] are *ca.* 0.1 Å shorter than the bonds with the external pyridine rings [average 1.976(6) Å]. The two [(dipic)$_2$Fe^{III}]$^-$ anion geometries are very similar to that observed in [(dipic)$_2$Fe^{III}]Na,[1] with, in particular, Fe−N and Fe−O ranging from 1.992(5) and 2.065(6) Å.

With tetrakis(2-pyridyl)pyrazine (tppz), a similar synthesis gave [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_2$. Curiously, recrystallization in water gave a different salt: [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_3$·(H$_3$O)·11H$_2$O (**5**). Dissolution of this salt in dichloromethane gave an insoluble pale green residue identified by FTIR spectroscopy as [(dipic)$_2$Fe^{II}](H$_5$O$_2$) by comparison with an authentic sample.[12]

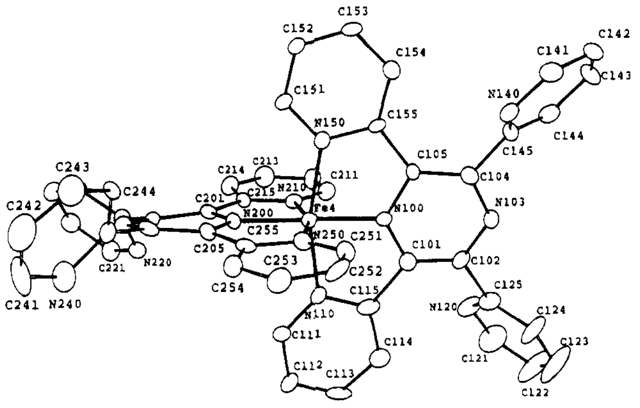

Figure 6. ORTEP drawing of the cation [Fe^{II}(tppz)$_2$]$^{2+}$ in **5**.

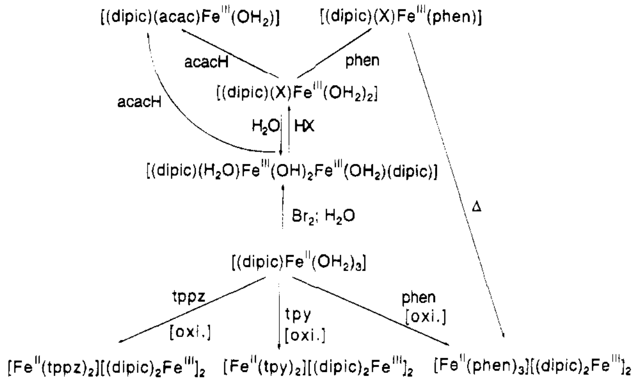

Figure 7. Syntheses from the complex [(dipic)Fe^{II}(OH$_2$)$_3$].

The asymmetric unit of [Fe^{II}(tppz)$_2$][(dipic)$_2$Fe^{III}]$_3$·(H$_3$O)·11H$_2$O contains one [Fe^{II}(tppz)$_2$]$^{2+}$ complex (Figure 6), three [(dipic)$_2$Fe^{III}]$^-$ counterions, and 12 molecules of water disordered over 23 crystallographic sites. Bond lengths and angles are presented in Table 11. The proton which is required for electroneutrality has been attributed for geometric reasons[13] to one of the 12 crystallization water molecules. Within [Fe^{II}(tppz)$_2$]$^{2+}$, the chelating parts of the ligands are nearly planar with the coordinated pyridine rings (7.3−8.2° out-of-plane with respect to the pyrazine rings). The two ligands are perpendicular with an angle of 91.9°. The uncomplexed pyridine rings are in staggered conformation with dihedral angles with respect to the pyrazine rings ranging from 50.1 to 59.8°. As observed in other iridium, zinc, and copper complexes of tppz[14] and in similar 2,3-bis(2-pyridyl)quinoxaline complexes,[15] the pyrazine rings are twisted by 5.2 and 5.9°. The structure shows some weak hydrogen bonds as indicated by the following distances: O(12)−H(611) = 2.04(2) Å and O(12)−O(610) = 2.89(2) Å; O(212)−H(601) = 1.81(2) Å and O(212)−O(600) = 2.88(2) Å; O(650)−H(681) = 1.94(3) Å and O(650)−O(680) = 2.67(4) Å; O(690)−H(731) = 2.16 Å and O(690)−O(730) = 2.98(3) Å.

Conclusion

All the iron(III) chemistry with dipic developed here comes from the mononuclear iron(II) precursor [(dipic)Fe^{II}(OH$_2$)$_3$].[1]

---

(11) Baker, A. T.; Goodwin, H. A. *Aust. J. Chem.* **1985**, *38*, 207.

(12) Hseu, J. F.; Chen, J. J.; Chuang, C. C.; Wei, H. H.; Cheng, M. C.; Wang, Y.; Yao, Y. D. *Inorg. Chim. Acta* **1991**, *184*, 1.

(13) Lainé, P.; Gourdon, A.; Launay, J.-P. *Inorg. Chem.* **1995**, *34*, 5138.

(14) (a) Vogler, L. M.; Scott, B.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 898. (b) Graf, M.; Greaves, B.; Stoeckli-Evans, H. *Inorg. Chim. Acta* **1993**, *204*, 239.

(15) Rillema, D. P.; Taghdiri, D. G.; Jones, D. S.; Keller, C. D.; Wrol, L. A.; Meyer, T. J.; Levy, H. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 578.

Figure 7 summarizes the principal results of this investigation. The oxidation of the precursor compound afforded the already known dinuclear bis(μ-hydroxo) iron(III) species [(dipic)(H_2O)Fe^{III}(μ-OH)$_2$$Fe^{III}$($OH_2$)(dipic)]. Its hydrolysis by an acid HX gave another key precursor, namely [(dipic)(X)Fe^{III}(OH_2)$_2$]. In the latter complex, the halide X^- and one water molecule can be substituted by the uninegatively charged bidentate ligand acac$^-$ to yield [(dipic)(acac)Fe^{III}(OH_2)]. If the reaction is performed with a neutral chelating ligand such as 1,10-phenanthroline, only the two water molecules of [(dipic)(X)-Fe^{III}(OH_2)$_2$] are displaced to give the corresponding halide complex [(dipic)(X)Fe^{III}(phen)]. Thermal degradation of this species induces a "redistribution" process of the ligands coupled with a partial reduction of the metal centers, which yielded a mixed-valence association [Fe^{II}(phen)$_3$][(dipic)$_2$$Fe^{III}$]$_2$ where [(dipic)$_2$$Fe^{III}$]$^-$ can be considered as a counterion. Similar compounds can be obtained by starting directly from [(dipic)-Fe^{II}(OH_2)$_3$] and the tridentate ligands tpy and tppz under oxidative (air) conditions.

Acknowledgment. The authors thank J. Bonvoisin (CEMES-CNRS, Toulouse, France) for his interest in our work and fruitful discussions.

Supporting Information Available: Complete tables of X-ray crystallographic parameters, atom coordinates, thermal parameters, bond lengths, and bond angles for complexes **1**–**5** (47 pages). Ordering information is given on any current masthead page.

IC950104O