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Bis(pyrazol-1-yl)acetates as Tripodal Heteroscorpionate Ligands in Iron Chemistry: Syntheses and Structures of Iron(II) and Iron(III) Complexes with bpza, bdmpza, and bd*t*bpza Ligands

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The molecular structure of the previously reported species "[Fe(bd*t*bpza)Cl]" has been revealed by X-ray structure determination to be a ferrous dimer $[Fe(bd\textit{t}bpza)Cl]_2$ (**2c**) [bd*t*bpza = bis(3,5-di-*tert*-butylpyrazol-1-yl)acetate]. The syntheses of ferrous 2:1 complexes $[Fe(bpza)_2]$ (**3a**) and $[Fe(bd\textit{t}bpza)_2]$ (**3c**) as well as ferric 1:1 complexes $[NEt_4][Fe(bpza)Cl_3]$ (**4a**) and $[NEt_4][Fe(bdmpza)Cl_3]$ (**4b**) [bpza = bis(pyrazol-1-yl)acetate, bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate] are reported. Complexes **3a**, previously reported $[Fe(bdmpza)_2]$ (**3b**), and **3c** are high-spin. No spin crossover to the low-spin state was observed in the temperature range of 5–350 K. **4a** and **4b** are synthesized in one step and in high yield from $[NEt_4]_2[Cl_3FeOFeCl_3]$. **4a** and **4b** are iron(III) high-spin complexes. Crystallographic information: **2c** ($C_{24}H_{39}ClFeN_4O_2\cdot CH_2Cl_2\cdot CH_3CN$) is triclinic, $P\bar{1}$, $a = 12.171(16)$ Å, $b = 12.851(14)$ Å, $c = 13.390(13)$ Å, $\alpha = 98.61(9)°$, $\beta = 113.51(11)°$, $\gamma = 108.10(5)°$, $Z = 2$; **3a** ($C_8H_7Fe_{0.5}N_4O_2$) is monoclinic, $P2_1/n$, $a = 7.4784(19)$ Å, $b = 7.604(3)$ Å, $c = 16.196(4)$ Å, $\beta = 95.397(9)°$, $Z = 4$; **3c** ($C_{24}H_{39}Fe_{0.5}N_4O_2$) is monoclinic, $P2_1/n$, $a = 9.939(6)$ Å, $b = 18.161(10)$ Å, $c = 13.722(8)$ Å, $\beta = 97.67(7)°$, $Z = 4$; **4b** ($C_{20}H_{35}Cl_3FeN_5O_2$) is monoclinic, $C2/c$, $a = 30.45(6)$ Å, $b = 12.33(2)$ Å, $c = 16.17(3)$ Å, $\beta = 118.47(5)°$, $Z = 8$.

Introduction

In the past decade protein structures of several mononuclear non-heme iron(II) enzymes were solved, such as isopenicillin N synthase (IPNS) (Figure 1), deacetoxycephalosporin C synthase (DAOCS), clavaminic acid synthase (CAS), proline 3-hydroxylase (P-3-H), taurine dioxygenase (TauD), and anthocyanidin synthase (ANS).[1−6]

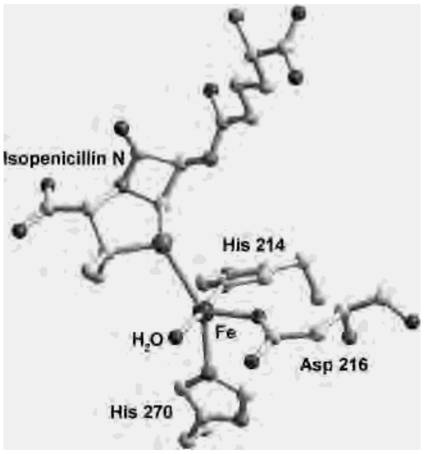

Figure 1. Active site of isopenicillin N synthase IPNS with IPN product (PDB code: 1QJE).[9a]

This increased structural information caused a growing interest in these enzymes[7] and especially in the iron binding facial 2-His-1-carboxylate triad, a term first introduced by

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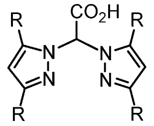

1a	bpzaH	R = H
1b	bdmpzaH	R = Me
1c	bd*t*bpzaH	R = *t*Bu

Figure 2. Bis(pyrazol-1-yl)acetic acids.

L. Que Jr.[8] This triad is found in many of these mononuclear non-heme iron(II) dependent enzymes.[7] The two iron binding histidines and one aspartate are conserved throughout the whole family of enzymes.[1a] Pseudo-kinetic X-ray diffraction experiments on IPNS showed several changes in the electron density close to the substrate but no changes to the 2-His-1-carboxylate facial triad during the catalytic cycle.[9] This implies a rather fixed geometry of these three iron binding amino acids and therefore a perfect target for a structural model complex.

Several model complexes for these enzymes have been investigated for more than 10 years.[7] Prominent examples are complexes with bulky hydridotris(pyrazol-1-yl)borato (Tp) ligands and models with tris(2-pyridylmethyl)amine (TPA) or TPA related ligands.[10,11] However, there was a lack of suitable *N*,*N*,*O*-tripod ligands with an anionic carboxylate donor that could mimic this triad properly. Recently we introduced bis(pyrazol-1-yl)acetato ligands (Figure 2) as suitable structural mimics for the facial 2-His-1-carboxylate triad.[12]

The first ferrous complexes with these monoanionic heteroscorpionate ligands were a 2:1 complex [Fe(bdmpza)$_2$] [bdmpza: bis(3,5-dimethylpyrazol-1-yl)acetate] and a species with the composition "[Fe(bd*t*bpza)Cl]" [bd*t*bpza: bis(3,5-di-*tert*-butylpyrazol-1-yl)acetate]. Initially it was not possible to distinguish between a monomeric and a dimeric constitution. We now report on the X-ray structural analysis that unambiguously proves a dimeric constitution [Fe(bd*t*bpza)-Cl]$_2$. The syntheses and structures of other ferrous 2:1 and ferric 1:1 complexes, accessible by a simple high-yield synthesis, are reported, too.

Experimental Section

General. All experiments were carried out in Schlenk tubes under argon atmosphere by using suitable purified solvents. Microcrystalline precipitates were separated by centrifugation with a Hettich Rotina 46 R Schlenk tube centrifuge or filtration. IR: Biorad FTS 60, CaF$_2$ cuvettes (0.5 mm), KBr matrix or PE pellet. EI MS and FAB MS: modified Finnigan MAT 312. Elemental analyses: Analytical Laboratory of the Fachbereich Chemie. Magnetic susceptibilities were measured at 5 kG using a Quantum Design MPMS XL SQUID magnetometer. Clear gelatin capsules were used as sample containers for measurements taken in the temperature range 5−350 K. The very small diamagnetic contribution of the gelatin capsule had a negligible contribution to the overall magnetization, which was dominated by the sample. Bis(pyrazol-1-yl)acetic acid (**1a**), bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**), and bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (**1c**) were synthesized from pyrazole, 3,5-dimethylpyrazole, and 3,5-di-*tert*-butylpyrazole as reported recently.[12,13] [NEt$_4$]$_2$[Cl$_3$FeOFeCl$_3$] was synthesized according to the literature method.[14]

[Fe(bd*t*bpza)Cl]$_2$, 2c. The iron(II) complex [Fe(bd*t*bpza)Cl]$_2$ (**2c**) was synthesized from water-free FeCl$_2$, potassium *tert*-butylate, and bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (**1c**) in acetonitrile as reported recently.[12] Crystallization from an acetonitrile/dichloromethane mixture yielded air-sensitive colorless crystals suitable for X-ray structure determination.

[Fe(bpza)$_2$], 3a. To a solution of bis(pyrazol-1-yl)acetic acid (**1a**) (500 mg, 2.60 mmol) in acetonitrile (20 mL) was added potassium *tert*-butylate (290 mg, 2.59 mmol), and the mixture was stirred vigorously for 30 min. FeCl$_2$ (170 mg, 1.34 mmol) was added, and the reaction mixture was stirred at ambient temperature for 4 h. The solvent was removed in vacuo. The pale green residue was washed with H$_2$O (2 × 20 mL) and dried in vacuo. Recrystallization from H$_2$O/MeOH yielded greenish blue crystals of **3a** suitable for X-ray structure determination. Yield: 320 mg (0.73 mmol, 56% according to KO^{t}Bu). Mp 285 °C (dec). $\mu_{\mathrm{eff}} = 5.12\ \mu_{\mathrm{B}}$ (5−350 K). FAB MS (NBOH): *m*/*z* (%) = 439 (100) [MH$^+$]. IR (KBr): $\nu_{\max}$ = 1653 s (as-CO$_2^-$), 1520 w (C(3)↔N(2)), 1508 w (C(3)↔N(2)), 1453 m (C(5)↔N(1)), 1401 m (C↔C), 1377 w, 1363 m (s-CO$_2^-$), 1353 w, 1290 m, 1281 w, 1246 m cm^{-1}. Calcd for C$_{16}$H$_{14}$FeN$_8$O$_4$ (438.2): C, 43.86; H, 3.22; N, 25.57. Found: C, 43.93; H, 3.28; N, 25.42.

[Fe(bd*t*bpza)$_2$], 3c. To a solution of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (**1c**) (420 mg, 1.01 mmol) in acetonitrile (20 mL) was added potassium *tert*-butylate (100 mg, 0.89 mmol), and the mixture was stirred vigorously for 20 min. Fe(BF$_4$)$_2$·6H$_2$O (160 mg, 0.47 mmol) was added, and the reaction mixture was stirred at ambient temperature for 6 h. The solvent was removed in vacuo.

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Table 1. Structure Determination Details of Compounds **2c**, **3a**, **3c**, and **4b**

	2c	**3a**	**3c**	**4b**
empirical formula	$C_{24}H_{39}ClFeN_4O_2{\cdot}CH_2Cl_2{\cdot}CH_3CN$	$C_8H_7Fe_{0.5}N_4O_2$	$C_{24}H_{39}Fe_{0.5}N_4O_2$	$C_{20}H_{35}Cl_3FeN_5O_2$
fw	632.87	219.10	443.53	539.73
cryst color/habit	colorless block	green block	amber plate	yellow block
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	12.171(16)	7.4784(19)	9.939(6)	30.45(6)
b, Å	12.851(14)	7.604(3)	18.161(10)	12.33(2)
c, Å	13.390(13)	16.196(4)	13.722(8)	16.17(3)
α, deg	98.61(9)	90	90	90
β, deg	113.51(11)	95.397(9)	97.67(7)	118.47(5)
γ, deg	108.10(5)	90	90	90
V, Å^3	1733(3)	916.9(5)	2455(3)	5338(18)
θ range, deg	2.05−27.00	2.53−26.99	2.24−27.01	2.08−25.00
H	−14 to 0	−9 to 9	−12 to 11	−36 to 36
K	−14 to 15	−9 to 8	−23 to 23	−14 to 14
L	−15 to 17	−20 to 20	−17 to 17	−18 to 19
Z	2	4	4	8
μ(Mo Kα), mm^{-1}	0.695	0.866	0.357	0.890
cryst size, mm	0.3 × 0.3 × 0.3	0.4 × 0.35 × 0.3	0.5 × 0.5 × 0.3	0.3 × 0.2 × 0.15
temp, K	241(2)	188(2)	245(2)	245(2)
reflns collected	7735	3859	10824	13347
indep reflns	7416	2010	5372	4705
obs reflns ($I > 2\sigma(I)$)	4571	1603	4323	3224
no. of parameters	343	133	277	280
R1 (obs)	0.0636	0.0324	0.0402	0.0518
R1 (overall)	0.1163	0.0457	0.0531	0.0851
wR2 (obs)	0.1482	0.0758	0.1017	0.1309
wR2 (overall)	0.1765	0.0815	0.1119	0.1515
diff peak/hole, e/Å^3	0.545/−0.628	0.272/−0.372	0.415/−0.474	0.468/−0.815

The brown residue was dissolved in dichloromethane (20 mL), filtered over Celite, and dried in vacuo to obtain a white solid. Crystals suitable for X-ray diffraction determination were obtained from an acetonitrile solution. Yield: 390 mg (0.44 mmol, 99% according to KO^{t}Bu). Mp 226 °C (dec). EI MS (70 eV, 240 °C): m/z (%) = 887 (0.5) [M$^+$], 786 (0.5) [M$^+$ − CO$_2$ − C$_4$H$_9$], 193 (54) [(C$_{11}$H$_{19}$N$_2$)CH$_2$], 57 (82) [C$_4$H$_9$]. IR (KBr): $\nu_{max} = 1679$ s (as-CO$_2^-$), 1548 w (C(3)$\leftrightarrow$N(2)), 1539 w (C(3)$\leftrightarrow$N(2)), 1480 w, 1464 w (C(5)$\leftrightarrow$N(1)), 1433 w, 1414 w, 1398 w, 1364 m (s-CO$_2^-$), 1332 m, 1302 w, 1249 w, 1218 w cm^{-1}. IR (CH$_2$Cl$_2$): $\nu_{max} = 1675$ s (as-CO$_2^-$), 1580 vw, 1545 m (C(3)$\leftrightarrow$N(2)), 1465 w cm^{-1}. Calcd for $C_{48}H_{78}FeN_8O_4$ (887.05): C, 64.99; H, 8.86; N, 12.63. Found: C, 64.61; H, 8.84; N, 12.43.

[NEt$_4$][Fe(bpza)Cl$_3$], 4a. To a solution of [NEt$_4$]$_2$[Cl$_3$FeOFeCl$_3$] (300 mg, 0.50 mmol) in CH$_3$CN (20 mL) was added bis(pyrazol-1-yl)acetic acid (**1a**) (192 mg, 1.00 mmol). The mixture was stirred for 10 min, filtered, and stored for 24 h at −30 °C. The microcrystalline precipitate was collected by filtration and dried in vacuo. Yield: 281 mg (0.58 mmol, 58%); mp 183 °C. $\mu_{eff} = 5.85$ μ_B (5−350 K). FAB MS (NBOH-matrix): m/z (%) = 352 (28) [M$^-$], 198 (80) [FeCl$_4^-$], 161 (75) [FeCl$_3^-$]. IR (KBr): $\nu_{max} = 1669$ s (as-CO$_2^-$), 1509 w (C(3)$\leftrightarrow$N(2)), 1483 w, 1445 w (C(5)$\leftrightarrow$N(1)), 1404 m (s-CO$_2^-$), 1309 w, 1282 w 1245 w cm^{-1}. Calcd for $C_{16}H_{27}Cl_3FeN_5O_2$ (483.63): C, 39.74; H, 5.63; N, 14.48. Found: C, 39.62; H, 5.74; N, 14.41.

[NEt$_4$][Fe(bdmpza)Cl$_3$], 4b. To a solution of [NEt$_4$]$_2$[Cl$_3$FeOFeCl$_3$] (421 mg, 0.70 mmol) in CH$_3$CN (20 mL) was added bis(3,5-dimethylpyrazol-1-yl)acetic acid (**1b**) (348 mg, 1.40 mmol). The mixture was stirred for 10 min, filtered, and stored for 24 h at −30 °C. The yellow crystalline precipitate was filtered off and dried in vacuo. Crystals suitable for X-ray structure determination were obtained from a solution of **4b** in acetonitrile at −30 °C. Yield: 306 mg (0.57 mmol, 41%). Mp 153 °C. $\mu_{eff} = 5.68$ μ_B (5−350 K). FAB MS (NBOH): m/z (%) = 373 (6) [C$_{12}$H$_{15}$N$_4$O$_2$FeCl$_2^-$], 198 (95) [FeCl$_4^-$], 161 (100) [FeCl$_3^-$]. - IR (CH$_2$Cl$_2$): $\nu_{max} = 1668$ s (as-CO$_2^-$), 1560 w (C(3)$\leftrightarrow$N(2)) cm^{-1}. IR (KBr): $\nu_{max} = 1657$ s (as-CO$_2^-$), 1559 m (C(3)$\leftrightarrow$N(2)), 1483 w, 1460 m (C(5)$\leftrightarrow$N(1)), 1417 w (C$\leftrightarrow$C), 1394 m (s-CO$_2^-$), 1333 w, 1318 w, 1247 w cm^{-1}. Crystals, calcd for $C_{20}H_{35}Cl_3FeN_5O_2$ (539.74): C, 44.51; H, 6.54; N, 12.98. Found: C, 44.44; H, 6.58; N, 12.91.

Calculations. Calculations were carried out by using GAMESS 6.2[15] running on Linux-2.4.10-SMP on two Pentium-II-400 dual-processor workstations parallelized with MPICH 1.2.3. The crystal structures of the iron complexes were used as starting geometry. Complete geometry optimizations were carried out on the implemented UHF/6-31G* basis set assuming high-spin state. The harmonic vibrational frequencies were calculated by the numerical evaluation of the second derivative of the molecular energy on the identical basis set. BdmpzaH was preoptimized using MM2 force-field, geometry completely optimized at RHF/6-31G* level, and the harmonic vibrational frequencies were calculated by the analytical evaluation of the second derivative of the energy.

X-ray Structure Determinations. A modified Siemens P4-diffractometer was used for data collection of single crystals of **2c**, **3a**, **3c**, and **4b** (graphite monochromator, Mo Kα radiation, $\lambda = 0.71073$ Å, scan rate 4−30°min^{-1} in ω). The structures were solved by direct methods (Siemens SHELXS-97) and refined with full-matrix least-squares against F^2 (Siemens SHELXL-97).[16] A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$. Hydrogen atoms were included in their calculated positions and refined in a *riding model*.

All details and parameters of the measurement are summarized in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC-202214 (**2c**), CCDC-202215 (**3a**), CCDC-202216 (**3c**), and CCDC-202217 (**4b**). Copies of the data can be obtained free

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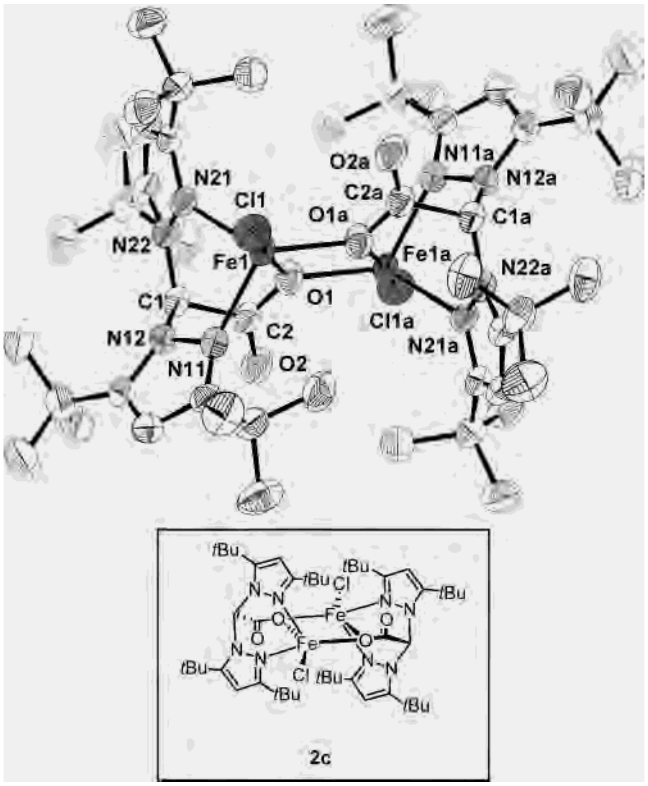
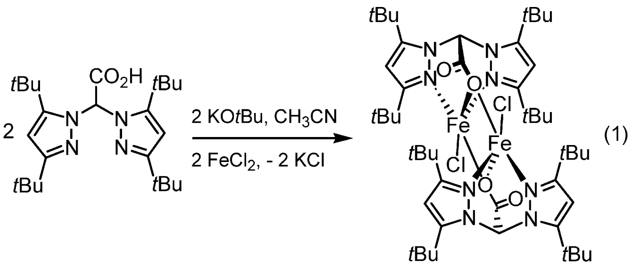


Figure 3. Molecular structure of [Fe(bd*t*bpza)Cl]$_2$ (**2c**). Thermal ellipsoids are drawn at the 50% probability level.

of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax, + 44−1223/336−033; E-mail, deposit@ccdc.cam.ac.uk). Structure pictures were prepared with the program Diamond 2.1e.[17]

Results and Discussion

Our recent investigations of the coordination properties of bis(pyrazol-1-yl)acetate ligands toward iron(II) indicated that the sterical hindrance of bis(3,5-dimethylpyrazol-1-yl)-acetic acid (bdmpzaH) (**1b**) is too small, resulting in 2:1 complexes [Fe(bdmpza)$_2$] (**3b**).[12] Reaction of the potassium salt of the sterically more demanding bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (bd*t*bpzaH) with FeCl$_2$ gave a 1:1 species “[Fe(bd*t*bpza)Cl]” according to elemental analysis.[12] Now we obtained crystals of the latter from acetonitrile/CH$_2$Cl$_2$. The X-ray structure determination reveals this species to be a dimer [Fe(bd*t*bpza)Cl]$_2$ (**2c**) (eq 1) (Figure 3).



1c **2c** (1)

Table 2. Selected Distances (Å) of the Complexes **2c**, **3a**, **3c**, and **4b**

	2c	**3a**	**3c**	**4b**
Fe−N(11)	2.172(4)	2.2054(17)	2.3400(17)	2.265(4)
Fe−N(21)	2.196(4)	2.1542(18)	2.353(2)	2.248(4)
Fe−O(1)	2.393(4)	2.0761(14)	2.0033(16)	2.049(4)
Fe−O(1a)	2.046(3)			
Fe−Cl(1)	2.320(4)			2.338(3)
Fe−Cl(2)				2.334(3)
Fe−Cl(3)				2.326(4)
Fe−Fe	3.670(4)			
O(2)−C(2)	1.227(5)	1.234(2)	1.233(2)	1.237(5)
O(1)−C(2)	1.307(5)	1.266(2)	1.284(2)	1.289(5)
C(1)−C(2)	1.559(5)	1.560(3)	1.561(3)	1.569(6)

Table 3. Selected Angles (deg) of the Complexes **2c**, **3a**, **3c**, and **4b**

	2c	**3a**	**3c**	**4b**
N(11)−Fe−N(21)	90.94(16)	86.43(6)	73.64(5)	80.86(18)
O(1)−Fe−N(11)	78.44(12)	84.60(6)	88.47(7)	82.64(16)
O(1)−Fe−N(21)	80.40(17)	83.89(6)	88.66(7)	81.07(18)
O(1)−Fe−Cl(1)	170.83(7)			91.14(14)
O(1a)−Fe−Cl(1)	103.94(16)			
O(1)−Fe−Cl(2)				91.10(17)
O(1)−Fe−Cl(3)				168.60(9)
N(11)−Fe−Cl(3)				90.29(13)
N(21)−Fe−Cl(1)	108.72(16)			91.52(17)
Cl(1)−Fe−Cl(2)				96.61(14)
Cl(1)−Fe−Cl(3)				94.74(12)
Cl(2)−Fe−Cl(3)				97.90(15)
Fe−O(1)−Fe	111.28(17)			

Relevant molecular distances and angles are listed in Tables 2 and 3. The geometry of the ferrous iron is trigonal bipyramidal. Thus, this structure confirms the tendency of iron complexes to coordination numbers higher than four. A related zinc complex [Zn(bd*t*bpza)Cl] shows a tetracoordinated and thus distorted tetrahedral geometry.[12] The two N-donors and one of the carboxylates of **2c** occupy the equatorial positions. In good agreement with the Kepert model[18] this equatorial Fe−O distance [2.046(3) Å] is much shorter than the axial Fe−O distance [2.393(4) Å]. The equatorial Fe−O bond is formed by the syn lone pair of the oxygen atom which is the most frequent binding lone pair in metal coordinating carboxylate donors.[7b] This bridging μ-acetato-κ*O*-binding mode might explain the asymmetric carboxylate IR absorption $\nu_{as} = 1681$ cm^{-1} which is 22 cm^{-1} higher than that of the previously reported [Fe(bdmpza)$_2$] (ν_{as}=1659 cm^{-1}).[12] The most striking feature of [Fe(bd*t*bpza)-Cl]$_2$ (**2c**) is the unusually long Fe−Fe distance of 3.670(4) Å. The CCDC database contains only two examples of dinuclear oxygen atom bridged iron complexes with similar long Fe−Fe distances [3.724(1)[19a] and 3.645(4) Å[19b]]. Complex **2c** is the only one of these three compounds with a pentacoordinated iron atom. This implies a possible relevance as a structural model for the active site of dinuclear iron enzymes such as methane monooxygenase (MMO) or ribonucleotide reductase (R2).[7]

A magnetic susceptibility study showed that **2c** follows the Curie law in the temperature range from 350 to 50 K

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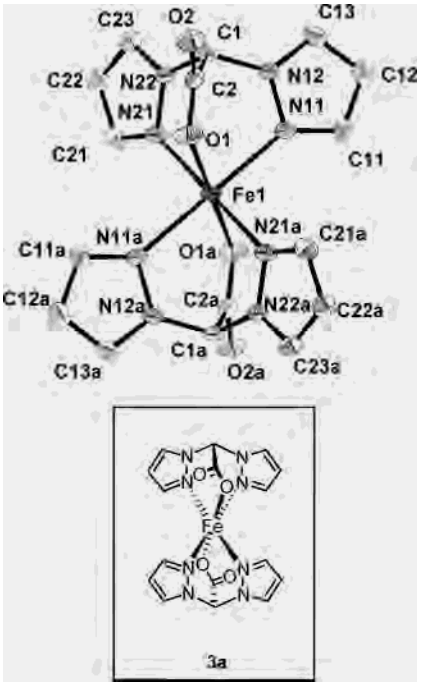

Figure 4. Molecular structure of [Fe(bpza)$_2$] (**3a**). Thermal ellipsoids are drawn at the 50% probability level.

with $\mu_{\mathrm{eff}} = 6.88\ \mu_{\mathrm{B}}$. Below 50 K there is a decrease of μ_{eff} although the data is not good enough for a detailed analysis. Such a behavior and similar μ_{eff} values in the range of 6.83−7.28 μ_{B} have been reported already by Lippard and co-workers for other diiron(II) complexes in which the coupling parameter J of an isotropic Heisenberg model ($\mathscr{H} = -2JS_1{\cdot}S_2$; $S_1 = S_2 = 2$) is close to zero.[20] Therefore, our data indicate the absence of significant magnetic exchange coupling in **2c**.

As mentioned above, the sterically less hindered bis(3,5-dimethylpyrazol-1-yl)acetic acid forms with FeCl$_2$ in a similar reaction a 2:1 complex [Fe(bdmpza)$_2$] (**3b**), which we reported recently.[12] We found a similar behavior for the even less hindered bis(pyrazol-1-yl)acetic acid (**1a**). The potassium salt of **1a** reacts with FeCl$_2$ to give [Fe(bpza)$_2$] (**3a**). The structure of [Fe(bpza)$_2$] (**3a**) (Figure 4) agrees well with that of [Fe(bdmpza)$_2$] (**3b**). Relevant distances and angles of **3a** are listed in Tables 2 and 3.

As in **3b** the anti lone pair of the carboxylate donor coordinates to the iron atom. Thus, the asymmetric carboxylate IR absorption ($\nu_{\mathrm{as}} = 1653$ cm^{-1}) appears at even lower wavenumbers compared to that of **3b**.

In order to assign more IR signals of **3a**, ab initio calculations on bdmpzaH (**1b**) and **3a** were performed. It is well-known for the chosen HF/6-31G* basis set that calculated harmonic vibrational frequencies are typically overestimated compared to experimental data. These errors arise from the neglect of anharmonicity effects, incomplete incorporation of electron correlation, and the use of finite basis sets in the theoretical treatment.[21] In order to achieve a correlation with observed spectra a scaling factor of approximately 0.84−0.91 has to be applied.[22] Depending on the examined vibration, this factor differs slightly even in the same molecule and is usually bigger for lower energies.[22] The results of the calculations are listed in Table 4.

Table 4. Observed and Calculated IR Absorptions (cm^{-1}) of **1b**, **3a**, and **4b**

	ν (obs)	ν (calcd)^b
1b	1747 (as-CO$_2$H)	2057
	1561 (C(3)↔N(2))^a	1791
	1442 (C(5)↔N(1))^a	1692, 1693
	1419 (C↔C)	1593
	1379	1555
	1344 (s-CO$_2$H)	1505
3a	1653 (as-CO$_2^-$)	1971, 1979
	1520, 1508 (C(3)↔N(2))^a	1737, 1741
	1453 (C(5)↔N(1))^a	1630
	1401 (C↔C)	1561
	1377	1537
	1363 (s-CO$_2^-$)	1502
4b	1657 (as-CO$_2^-$)	1971
	1559 (C(3)↔N(2))^a	1768, 1772
	1460 (C(5)↔N(1))^a	1685
	1417 (C↔C)	1591
	1394 (s-CO$_2^-$)	1562

^{a} Numbering refers to the position of the atom in the pyrazolyl ring. ^{b} Scale factors range from 0.84 to 0.91.

The calculations were calibrated on the asymmetric carboxylate ν_{asym} at 1653 cm^{-1}. This value is in good agreement with the values observed previously for related bis(pyrazol-1-yl)acetato complexes.[13]

We were especially interested in the symmetric carboxylate vibration ν_{sym} because pursuant to literature the difference $\Delta(\nu_{\mathrm{asym}} - \nu_{\mathrm{sym}})$ for a unidentate carboxylate group should be ≥ 200 cm^{-1}.[23] For several related transition metal bis(pyrazol-1-yl)acetato and bis(3,5-dimethylpyrazol-1-yl)acetato complexes, absorptions around 1460 cm^{-1} have been assigned to ν_{sym}.[13d,24] But, according to our calculations, this absorption at 1453 cm^{-1} is caused by a C(5)↔N(1) vibration (numbering refers to the position in the pyrazolyl ring). This is confirmed by a similar IR absorption of 3,5-dimethylpyrazol-1-ylmethane (1451 cm^{-1}). Instead the calculation predicts a symmetric carboxylate vibration ν_{sym} at 1350 cm^{-1}. The recently published complex [Cu(bdmpza)$_2$] for which ν_{sym} was unambiguously assigned to this region of the spectrum supports this.[25] These considerations imply a $\Delta(\nu_{\mathrm{asym}} - \nu_{\mathrm{sym}})$ around 300 cm^{-1} for the group of unidentate bis(pyrazol-1-yl)acetato ligands.

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The **3a** related complex {Fe[HB(pz)$_3$]$_2$}, which has been investigated for many years, has at ambient temperature a low-spin t_{2g}^6 configuration.[26] It is purple and the average Fe−N distance is 1.975 Å at 289 K.[26] Upon heating, {Fe[HB(pz)$_3$]$_2$} exhibits at 393 K a spin crossover[27] to a $t_{2g}^4e_g^2$ high-spin state, and its color changes from purple to white.[26] {Fe[HB(3,5-Me$_2$pz)$_3$]$_2$}, a similar complex with the more bulky [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand, is at ambient temperature a colorless high-spin complex.[26] Upon cooling below 200 K it changes gradually to a low-spin state.[26] Usually the Fe−N distances in ferrous high-spin complexes are 0.2 Å longer compared to those in low-spin complexes. For example, for {Fe[HB(3,5-Me$_2$pz)$_3$]$_2$} an average Fe−N distance of 2.17 Å has been reported.[26] Similar results were published recently for {Fe[HC(pz)$_3$]$_2$}$^{2+}$ and {Fe[HC(3,5-Me$_2$pz)$_3$]$_2$}$^{2+}$.[28] The Fe−N distances of **3a** (at 188 K) [2.2054(17) and 2.1542(18) Å] are significantly longer compared to those of {Fe[HB(pz)$_3$]$_2$}. These Fe−N distances and the lack of a purple or red color indicate that **3a** is a ferrous high-spin complex at ambient temperature. Upon cooling in liquid nitrogen the white to pale green crystal powder of **3a** showed no change of color. Magnetic susceptibility studies of **3a** and **3b** indicate that both samples are high-spin and obey the Curie law in the temperature range 5−350 K with μ_{eff} of 5.12 μ_B (**3a** and **3b**). Therefore, a spin crossover upon cooling can be excluded so far.

In attempts to synthesize an acetato complex [Fe(bd*t*bpza)(OAc)] from K[bd*t*bpza], Fe[ClO$_4$]$_2$, and NaOAc we observed the formation of a 2:1 complex [Fe(bd*t*bpza)$_2$] (**3c**) as a byproduct. Without adding NaOAc and by using Fe[BF$_4$]$_2$·6H$_2$O, pure **3c** was obtained. Similar results were obtained for the reaction of [Fe(OAc)$_2$] with **1c**. The molecular structure of **3c** is shown in Figure 5. Relevant molecular distances and angles are listed in Tables 2 and 3.

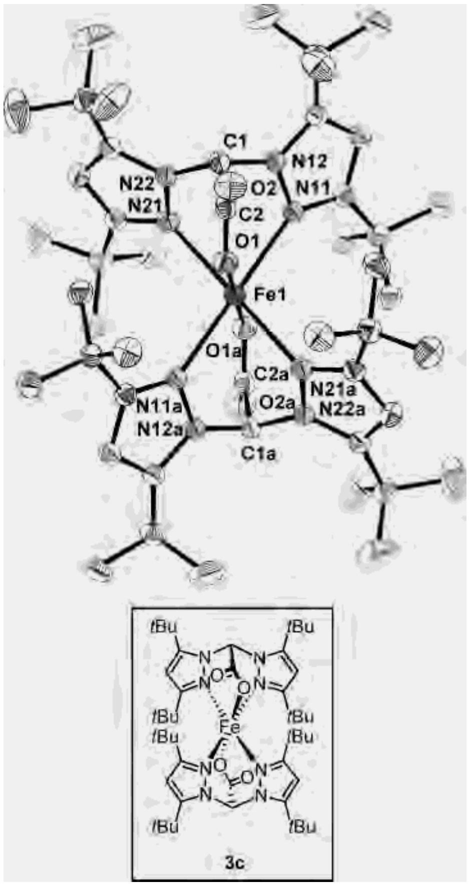
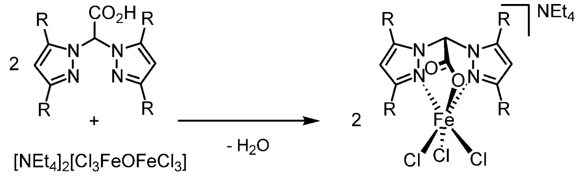


Figure 5. Molecular structure of [Fe(bd*t*bpza)$_2$] (**3c**). Thermal ellipsoids are drawn at the 50% probability level.

Due to the bulky ligand the Fe−N distances of **3c** [2.3400(17) and 2.353(2) Å] are much longer than those of **3a** and **3b** [**3b**: 2.169(3) and 2.212(3) Å].[12] This causes a weak ligand field and makes a crossover to low-spin state very unlikely. The pale amber to white color and these Fe−N distances indicate again the high-spin state of **3c**. The IR signals were assigned according to **3a**.

Despite several attempts we were unable to obtain paramagnetic NMR spectra of **3a** or **3c** probably due to the low solubility of the complexes. All three [FeL$_2$] complexes are stable under aerobic conditions even at $T > 200$ °C.

We subsequently focused on iron(III) complexes. Reaction of the iron(III) precursor [NEt$_4$]$_2$[Cl$_3$FeOFeCl$_3$][14] with bpzaH (**1a**) or bdmpzaH (**1b**) yielded 2 equiv of [NEt$_4$][Fe(bpza)Cl$_3$] (**4a**) and [NEt$_4$][Fe(bdmpza)Cl$_3$] (**4b**) by the loss of 1 equiv of water (eq 2). The structure of **4b** is depicted in Figure 6. Selected molecular distances and angles are listed in Tables 2 and 3.



(2)

1a (R = H), **1b** (R = Me) **4a** (R = H), **4b** (R = Me)

The synthesis of the similar complexes [NEt$_4$][FeLCl$_3$] [L = HB(pz)$_3$ and HB(3,5-Me$_2$pz)$_3$] from [NEt$_4$]$_2$[Cl$_3$FeOFeCl$_3$] and K[HB(pz)$_3$] or K[HB(3,5-Me$_2$pz)$_3$] has been reported earlier.[29] The Fe−Cl distances [2.326(4), 2.334(3), and 2.338(3) Å] agree well with those reported for [NEt$_4$][Fe(HB(pz)$_3$)Cl$_3$] [2.335(2), 2.325(2), and 2.291(2) Å].[29] Due to the methyl groups at C3 and C5 of the pyrazoles the Fe−N

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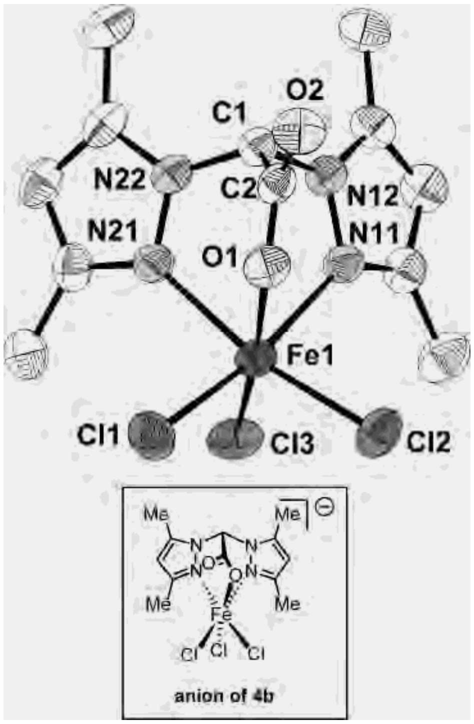

Figure 6. Molecular structure of the anion $[Fe(bdmpza)Cl_3]^-$ of **4b**; NEt_4^+ cation omitted for better view. Thermal ellipsoids are drawn at the 50% probability level.

distances [2.248(4) and 2.265(4) Å] are slightly longer than those of $[NEt_4][Fe(HB(pz)_3)Cl_3]$ [2.175(5), 2.152(4), and 2.152(4) Å].[29]

The IR signals of **4b** were assigned by performing ab initio calculations on **4b** as described above (Table 4). Again the symmetric carboxylate absorption $\nu_{sym}(CO_2^-)$ (1394 cm^{-1}) is found at rather low energy, giving a difference $\Delta(\nu_{asym} - \nu_{sym})$ of ~260 cm^{-1}. The IR signals of **4a** were assigned according to the signals of **4b**.

4a and **4b** show Curie law behavior with μ_{eff} of 5.85 μ_B (**4a**) and μ_{eff} of 5.68 μ_B (**4b**). These values are in good agreement with $t_{2g}{}^3e_g{}^2$ high-spin iron(III). Since no alkali bis(pyrazol-1-yl)acetates but the pure acids bpzaH (**1a**) and bdmpzaH (**1b**) are used in these syntheses, **4a** and **4b** are obtained in high yield and purity. No side reaction to ferric 2:1 complexes has been observed so far, as it was reported by Kim et al. for $[NEt_4][Fe(HB(pz)_3)Cl_3]$.[30] The formation of $[NEt_4][Fe(bd\textit{t}bpza)Cl_3]$ in a reaction of the sterically hindered bd*t*bpzaH (**1c**) with $[NEt_4]_2[Cl_3FeOFeCl_3]$ was not observed.

Conclusion

The molecular structure of the species "[Fe(bd*t*bpza)Cl]" is by X-ray structure analysis unambiguously revealed to be a ferrous dimer $[Fe(bd\textit{t}bpza)Cl]_2$ (**2c**) with bridging oxygen atoms and a trigonal bipyramidal geometry at the iron atoms. This dimer can be interpreted as two disfavored tetracoordinated "[Fe(bd*t*bpza)Cl]" species, which are now stabilized by this bridging oxygen and by the formation of more favored pentacoordinated iron centers. A penta- or hexacoordinated monomeric complex $[Fe(bd\textit{t}bpza)Cl(solv)_n]$ (n = 1,2) would mimic the facial 2-His-1-carboxylate triad of nonheme iron dependent oxygenases and oxidases by the two pyrazolyl groups and the carboxylate of the bd*t*bpza ligand. Future experiments will therefore focus on attempts to split this ferrous dimer to such solvated complexes in order to obtain good structural models. Monomeric ferric 1:1 complexes $[NEt_4][Fe(bpza)Cl_3]$ (**4a**) and $[NEt_4][Fe(bdmpza)Cl_3]$ (**4b**) are synthesized in one step and in high yield from $[NEt_4]_2[Cl_3FeOFeCl_3]$. The structure of **4b** shows a binding mode of the two pyrazolyl groups and the carboxylate of bdmpza that is very similar to that of the two histidines and the aspartate or glutamate in the facial 2-His-1-carboxylate triad. Thus the ferric complexes **4a** and **4b** might be useful precursors on the way to model complexes with natural substrates.

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