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Unusual Nitrite Complexes of Iron(III) and Iron(II) Stabilized by the Tris(3,5-dimethylpyrazolyl)borate Ligand

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Halide metathesis with silver nitrite allows for either stepwise or complete substitution of all three chloride ligands in the iron(III) compound $[NEt_4][HB(3,5\text{-}Me_2pz)_3FeCl_3]$ (**1**) to give the complexes $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)_xCl_{3-x}]$, $x = 1-3$ (**2**−**4**), and $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(\eta^2\text{-}ONO)Cl]$ (**5**), which were characterized by elemental analyses, electrochemistry, and IR, EPR, and UV−vis spectroscopy. Single-crystal X-ray diffraction was used to characterize the ferric complexes **2** and **4** and the ferrous chelating nitrito complex **5**. The crystal structures of the ferric complexes exhibit monodentate, O−bound nitrito ligands, while the change in metal oxidation state from +3 to +2 leads to a chelating nitrito ligand in **5**.

Introduction

Despite the well-established coordination chemistry of the nitrite ligand with various transition metals,[1] only a few examples for nitrite coordination to iron centers have been reported.[2] The chemistry of the iron−nitrite system is still largely unexplored, mainly because of the lack of accessible and well-characterized ferric and ferrous nitrite compounds.[3] For example, reactions of aqueous solutions of ferrous or ferric chloride with nitrite salts only yield mixtures of iron oxides and nitrate and so far no simple ferrous or ferric nitrite salts such as $Fe(NO_2)_2$ or $Fe(NO_2)_3$ have been isolated.[4]

The ability of the hydrotris(1-pyrazolyl)borate ligand to stabilize complexes with otherwise elusive ligand sets has been demonstrated for various transition metal compounds.[5] In addition, many of these complexes are models for non-heme iron metalloenzymes with multiple nitrogen coordination.[5b,6] In this paper we report the synthesis and characterization of anionic ferrous and ferric hydrotris(3,5-dimethyl-1-pyrazolyl)borate complexes bearing O-bound nitrito and chelating nitrito ligands. Our results demonstrate that remarkably stable ferric complexes, containing up to three nitrito ligands, can be easily synthesized via chloride/nitrite metatheses from $[NEt_4][HB(3,5\text{-}Me_2pz)_3FeCl_3]$ (**1**) and silver nitrite. We also show that the coordination mode of the nitrite ligand, O-bound nitrito versus chelating nitrito, can be easily altered by the oxidation state of the iron center.

Experimental Section

All reactions were performed either in an inert-atmosphere glovebox or by standard Schlenk-line techniques. Solvents were freshly distilled under nitrogen from appropriate drying agents before use. EPR spectra were measured in acetonitrile at 4.2 K on either a Bruker ESP 300 or an EMX spectrometer. All other instrumental methods have been described before.[7]

The starting complex $[NEt_4][HB(3,5\text{-}Me_2pz)_3FeCl_3]$ (**1**) was synthesized by the published method of Fukui et al. from $[NEt_4]_2[Cl_3Fe-O-FeCl_3]$ and $K[HB(3,5\text{-}Me_2pz)_3]$, KL.[10] All other reagents were obtained commercially and used as supplied.

Synthesis of $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)Cl_2]$ (2). To a solution of 50.0 mg (0.085 mmol) of $[NEt_4][HB(3,5\text{-}Me_2pz)_3FeCl_3]$ (**1**) in 30 mL of acetonitrile was added 13.1 mg (0.085 mmol) of $AgNO_2$ in 10 mL of acetonitrile and the mixture was stirred for 45 min at room temperature. The dark red solution was filtered from precipitated AgCl. After 24 h, the solution was filtered for a second time from additional small amounts of precipitated AgCl and the solvent allowed to evaporate slowly to yield 47.0 mg (92%) of dark red, air-stable crystals of the nitrito complex **2**. Anal. Calcd for $C_{23}H_{42}BCl_2FeN_8O_2{\cdot}0.5CH_3CN$: C, 46.36; H, 7.07; N, 19.14. Found: C, 46.13; H, 6.86; N, 19.25.

Synthesis of $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)_2Cl]$ (3). In a preparation similar to that for **2**, 50.0 mg (0.085 mmol) of **1** and 26.2 mg (0.17 mmol) of $AgNO_2$ yielded 45.0 mg (87%) of dark red, air-stable crystals of the bis(nitrito) complex **3**. Anal. Calcd for $C_{23}H_{42}BClFeN_9O_4{\cdot}0.5CH_3CN$: C, 45.65; H, 6.96; N, 21.07. Found: C, 44.83; H, 6.66; N, 21.83.

Synthesis of $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)_3]$ (4). In a similar preparation, 50.0 mg (0.085 mmol) of **1** and 39.2 mg (0.255 mmol) of $AgNO_2$ yielded 48.0 mg (91%) of dark red, air-stable crystals of the tris(nitrito) complex **4**. Anal. Calcd for $C_{23}H_{42}BFeN_{10}O_6$: C, 44.46; H, 6.92; N, 22.53. Found: C, 44.53; H, 7.01; N, 22.56.

Synthesis of $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(\eta^2\text{-}ONO)Cl]$ (5). Method 1. A mixture of 50.0 mg (0.085 mmol) $[NEt_4][LFeCl_3]$ (**1**) and 11 mg (0.090 mmol) of $Na_2N_2O_3$ (Angeli's salt) in 30 mL of acetonitrile was stirred for 4 h. The orange solution was filtered off and the solvent removed under vacuum. Recrystallization from acetonitrile yielded 32.0 mg (68%) of **5** as orange crystals. Anal. Calcd for $C_{23}H_{42}BClFeN_8O_2$: C, 48.91; H, 7.51; N, 19.97. Found: C, 48.07; H, 6.96; N, 19.55.

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Table 1. Crystallographic Data for **2**, **4**, and **5**

	2	**4**	**5**
formula	$C_{23}H_{42}BCl_2FeN_8O_2$	$C_{23}H_{42}BFeN_{10}O_6$	$C_{23}H_{42}BClFeN_8O_2$
fw	600.21	621.31	564.76
a (Å)	10.449(2)	15.623(3)	18.214(4)
b (Å)	10.449(2)	12.189(2)	16.325(3)
c (Å)	24.5700(10)	10.064(2)	19.508(4)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	120	125.75(3)	90
V (Å^3)	2323.2(6)	1555.3(5)	5801(2)
Z	3	2	8
space group	*R*3	*Cm*	*Pbca*
D_c (g/cm^3)	1.285	1.325	1.293
T (°C)	20	20	20
radiation, *λ* (Å)	Mo K_α, 0.710 73	Mo K_α, 0.710 73	Mo K_α, 0.710 73
μ (mm^{-1})	0.693	0.537	0.646
2*θ* limits (deg)	5.6−48.0	4.6−50.0	4.2−45.0
no. of unique data	816	1498	3796
no. of parameters	128	212	325
R1[a]	0.0638	0.0521	0.0660
wR2[b]	0.1783	0.1384	0.1401

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Method 2. A 20 mg sample of $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)Cl_2]$ (**2**) (0.033 mmol) was stirred in 20 mL of acetonitrile with excess Hg/Zn for 3 h. Filtration and removal of the solvent yielded **5** in almost quantitative yield as determined by UV−Vis and IR spectroscopy.

Synthesis of $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO_2)Cl_2]$ (6). In a preparation similar to that for **2**, 50.0 mg (0.085 mmol) of **1** and 14.4 mg (0.085 mmol) of $AgNO_3$ yielded 50.0 mg (95%) of dark red, air-stable crystals of the mono(nitrato) complex **6**. Anal. Calcd for $C_{23}H_{42}BCl_2FeN_8O_3$: C, 44.75; H, 6.87; N, 18.15. Found: C, 44.33; H, 6.81; N, 18.50.

X-ray Crystallographic Methods: $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)Cl_2]$ (2), $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)_3]$ (4), and $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(\eta^2\text{-}ONO)Cl]$ (5). Suitable crystals were obtained by slow evaporation of acetonitrile solutions. Diffraction data were collected on a Siemens P4 diffractometer. The unit cell parameters were obtained by least-squares refinements of 25 accurately centered high-angle reflections.

The structures were solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures using SHELXTL and the SHELX-95 package.[8] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions with fixed coordinates and thermal parameters. Absorption corrections were not necessary. Crystal data and details of the structure determinations are summarized in Table 1, bond lengths and angles in Table 2, and atomic coordinates in Tables 3−5. Compounds **2** and **4** crystallize in the noncentric space groups *R*3 and *Cm*. The absolute configuration for **4** was successfully determined by refining the Flack parameter (1.06(6)).[9] On the other hand, possibly due to the presence of nitrite/chloride ligand disorder in **2**, its absolute configuration could not be satisfactorily determined, and the final refinement returned a Flack parameter of 0.16(9).[9]

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**, **4**, and **5**

	$[NEt_4][LFe(ONO)Cl_2]$, **2**		
Fe(1)−N(1)	2.188(12)	O(1)−N(3)-O(2)	139(8)
Fe(1)−O(1)	1.72(4)	N(3)−O(1)−Fe(1)	116(3)
Fe(1)−Cl(1)	2.343(9)	Cl(1)−Fe(1)−Cl(2)	97.0(4)
N(3)−O(1)	1.44(8)		
N(3)−O(2)	0.97(9)		
	$[NEt_4][LFe(ONO)_3]$, **4**		
Fe(1)−N(1)	2.134(5)	O(1)−N(5)−O(2)	114.2(10)
Fe(1)−N(3)	2.127(8)	O(3)−N(6)−O(4)	116(2)
Fe(1)−O(1)	1.980(5)	N(5)−O(1)−Fe(1)	124.6(6)
Fe(1)−O(3)	1.996(8)	N(6)−O(3)−Fe(1)	120.6(8)
N(5)−O(1)	1.274(11)	O(1)−Fe(1)−O(3)	92.4(2)
N(5)−O(2)	1.206(11)	O(1)−Fe(1)−O(#1)	88.9(3)
N(6)−O(3)	1.293(14)		
N(6)−O(4)	1.12(2)		
	$[NEt_4][LFe(\eta^2\text{-}ONO)Cl]$, **5**		
Fe(1)−N(1)	2.110(6)	O(1)−N(7)−O(2)	113.2(8)
Fe(1)−N(3)	2.296(6)	N(7)−O(1)−Fe(1)	94.5(6)
Fe(1)−N(5)	2.098(6)	N(7)−O(2)−Fe(1)	94.6(6)
Fe(1)−Cl(1)	2.429(3)	O(1)−Fe(1)−O(2)	57.5(3)
Fe(1)−O(1)	2.190(6)	O(1)−Fe(1)−Cl(1)	92.3(2)
Fe(1)−O(2)	2.195(6)	O(2)−Fe(1)−Cl(1)	92.6(2)
N(7)−O(1)	1.270(10)		
N(7)−O(2)	1.258(10)		

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **2**

atom	*x*	*y*	*z*	*U*(eq)
Fe(1)	10000	10000	−1452(8)	84(1)
N(3)	8716(65)	8274(61)	−2326(33)	149(16)
O(2)	8060(102)	7578(95)	−2595(36)	255(30)
O(1)	9088(42)	8290(46)	−1760(20)	127(12)
Cl(1)	8704(42)	7771(12)	−1931(10	163(4)
N(1)	11051(14)	11841(13)	−878(9)	96(3)
C(3)	9127(19)	7282(20)	2862(12)	142(5)
C(2)	8426(21)	6242(21)	3268(12)	150(7)
N(2)	10873(11)	11553(11)	−331(9)	105(3)
C(4)	8668(19)	6657(17)	2388(11)	127(4)
C(6)	8129(97)	6440(137)	3868(6)	179(14)
C(6A)	8701(108)	6281(147)	6886(5)	179(14)
C(7)	9081(30)	7370(19)	1867(13)	188(9)
B(1)	10000	10000	−123(11)	84(6)
N(4)	6667	3333	−658(10)	86(3)
C(11)	6667	3333	−1712(28)	209(13)
C(21)	7119(114)	2795(143)	−1108(25)	217(15)
C(12)	6667	3333	9(120)	209(13)
C(22)	7413(317)	2614(330)	−446(84)	217(15)
C(13)	7919(87)	2492(80)	44(33)	209(13)
C(23)	7715(82)	3913(75)	−226(25)	217(15)
C(14)	6622(65)	5521(50)	−159(24)	209(13)
C(24)	6135(59)	4333(56)	−714(4)	217(15)
C(11)	3738(14)	5000	13203(26)	106(5)
C(12)	5014(20)	5000	13710(33)	162(12)
C(13)	3028(11)	4013(9)	10676(19)	104(4)
C(14)	2991(10)	2931(8)	11546(22)	113(5)
C(15)	1854(12)	5000	11158(19)	79(4)
C(16)	1009(10)	5000	9450(18)	78(3)

Results and Discussion

Synthesis. Three new anionic ferric complexes with up to three nitrito ligands were synthesized according to eq 1. This class of complexes have a common precursor, $[NEt_4][HB(3,5\text{-}Me_2pz)_3FeCl_3]$ (**1**), synthesized from $[NEt_4]_2[Cl_3Fe{-}O{-}FeCl_3]$ and $K[HB(3,5\text{-}Me_2pz)_3]$, KL.[10] As expected, the chloride ligands in **1** can be stepwise exchanged by nitrite. Employing the correct stoichiometric amounts of silver nitrite is crucial to obtain the pure mono- and bis(nitrito) complexes **2**−**4**. Chloride substitution proceeds step by step, which has been demonstrated by converting the mono(nitrito) complex **2** into either the bis- or tris(nitrito) complex **3** or **4** by treating it with an additional 1 or 2 equiv of silver nitrite.

Stability and Reactivity Studies. The nitrito complexes **2**−**4** (Figures 2 and 3) were found to be surprisingly air stable. The solids can be stored in the presence of atmospheric oxygen, and in solution no adventitious oxidation of the nitrite ligand to nitrate has been observed. The formation of ferric nitrate complexes was ruled out by independently synthesizing the

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**

atom	x	y	z	U(eq)
Fe(1)	930(1)	8793(1)	1436(1)	41(1)
Cl(1)	268(1)	9653(1)	2242(1)	62(1)
N(1)	1355(4)	7998(4)	2190(3)	39(2)
N(2)	1256(3)	7170(4)	2093(3)	40(2)
N(3)	1525(4)	7924(4)	696(3)	41(2)
N(4)	1423(4)	7104(4)	821(3)	40(2)
N(5)	37(4)	8012(4)	1249(3)	42(2)
N(6)	143(4)	7181(4)	1297(3)	40(2)
N(7)	1477(6)	10075(5)	814(5)	77(3)
N(8)	657(4)	12532(4)	1368(4)	48(2)
O(1)	883(4)	9729(4)	633(3)	64(2)
O(2)	1798(4)	9709(4)	1295(4)	64(2)
C(1)	1725(5)	8082(5)	2769(5)	47(2)
C(2)	1868(5)	7335(6)	3053(5)	56(3)
C(3)	1584(5)	6755(5)	2617(4)	48(2)
C(4)	1941(5)	8923(6)	3024(5)	70(3)
C(5)	1580(6)	5838(5)	2668(5)	72(3)
C(6)	1986(5)	7948(5)	155(4)	43(2)
C(7)	2151(5)	7166(5)	−63(4)	50(2)
C(8)	1793(5)	6639(5)	369(4)	45(2)
C(9)	2233(5)	8747(5)	−152(5)	61(3)
C(10)	1775(5)	5728(5)	370(5)	61(3)
C(11)	−668(5)	8126(5)	1083(5)	51(2)
C(12)	−1013(5)	7362(5)	1030(5)	60(3)
C(13)	−491(5)	6789(6)	1158(4)	55(3)
C(14)	−548(6)	5861(5)	1151(5)	76(3)
C(15)	−983(5)	8960(5)	973(5)	64(3)
C(16)	743(6)	12116(8)	2052(6)	92(4)
C(17)	1469(7)	11590(7)	2099(6)	108(5)
C(18)	−4(6)	13081(7)	1427(7)	89(4)
C(19)	−197(7)	13564(7)	774(7)	115(5)
C(20)	1325(6)	13013(7)	1193(6)	88(4)
C(21)	1511(7)	13687(7)	1735(7)	118(5)
C(22)	554(6)	11910(7)	803(5)	84(4)
C(23)	−147(5)	11404(6)	848(6)	80(3)
B(1)	912(5)	6839(5)	1420(5)	42(2)

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**

atom	x	y	z	U(eq)
Fe(1)	640(1)	5000	4351(1)	30(1)
N(1)	395(4)	6159(4)	2570(5)	30(1)
N(2)	−454(4)	6028(4)	954(5)	33(1)
N(3)	−1029(6)	5000	3039(9)	36(2)
N(4)	−1668(6)	5000	1347(9)	33(2)
N(5)	288(8)	2973(7)	5472(13)	88(3)
N(6)	2874(9)	5000	6890(15)	74(3)
N(7)	3020(7)	5000	11602(11)	52(2)
O(1)	814(5)	3863(5)	5896(7)	56(1)
O(2)	490(10)	2406(7)	6603(15)	136(4)
O(3)	2178(6)	5000	5319(9)	50(2)
O(4)	3723(8)	5000	7368(19)	140(6)
B(1)	−1162(6)	5000	446(9)	31(2)
C(1)	−498(5)	6868(5)	62(6)	39(1)
C(2)	334(5)	7562(6)	1089(7)	44(1)
C(3)	872(5)	7104(5)	2645(8)	39(1)
C(4)	−1353(7)	6993(6)	−1759(8)	60(2)
C(5)	1836(6)	7505(6)	4189(8)	54(2)
C(6)	−2700(7)	5000	778(12)	39(2)
C(7)	−2744(7)	5000	2086(12)	43(2)
C(8)	−1698(6)	5000	3507(10)	36(2)
C(9)	−3585(7)	5000	−1035(13)	61(3)
C(10)	−1324(8)	5000	5199(13)	55(2)
C(11)	3738(14)	5000	13203(26)	106(5)
C(12)	5014(20)	5000	13710(33)	162(12)
C(13)	3028(11)	4013(9)	10676(19)	104(4)
C(14)	2991(10)	2931(8)	11546(22)	113(5)
C(15)	1854(12)	5000	11158(19)	79(4)
C(16)	1009(10)	5000	9450(18)	78(3)

$$\underset{\mathbf{1}}{[NEt_4][HB(3,5\text{-}Me_2pz)_3FeCl_3]} + xAgNO_2 \rightarrow \underset{\mathbf{2-4}\ (x = 1-3)}{[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)_xCl_{3-x}]} + xAgCl \quad (1)$$

ferric nitrato compound $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO_2)Cl_2]$ (**6**) from (**1**) and silver nitrate. Comparison of the IR spectroscopic data for the nitrite and nitrate derivatives, Table 6, is consistent with a η^1-O-bound ligand in each case.[11] Surprisingly, we were not able to transform the ferric nitrito moiety in **2** to a ferrous nitrosyl group either by acid-catalyzed reduction of **2**, a reaction that frequently results in the formation of ferrous nitrosyls,[12] or by reduction with Zn/Hg. Reducing **2** with Zn/Hg results in formation of the anionic ferrous complex, **5**, in which the nitrito ligand replaces one of the chlorides and adopts a chelating nitrito mode. Preferential chelating nitrito coordination in this system is further demonstrated in the reaction of **1** with $Na_2N_2O_3$ (Angeli's salt) as illustrated in Scheme 1. A ferrous nitrosyl complex was the anticipated product from this reaction, as has been found for the ferric heme type compounds with Angeli's salt;[13] but, instead, again the chelating ferrous nitrito complex **5**, was isolated in good yield.

Physical Properties of the Complexes. Spectroscopic and electrochemical data are summarized in Table 6. The IR spectra of **2**−**4** exhibit three intense bands typical for O-bound, nitrito groups at ν_{asym} 1440−1470 cm^{-1}, ν_{sym} 980−1020 cm^{-1}, and δ 800−810 cm^{-1}.[11] To confirm these assignments the ^{15}N derivative of **2** has been prepared, and as expected, the IR active ν_{sym} and ν_{asym} bands are shifted by 28 and 30 cm^{-1}, respectively, to lower frequencies. For the chelating nitrito group in **5** the ν_{asym} band is observed at 1484 cm^{-1}. The UV−vis spectroscopic features of **4** and **6** are similar to those of the starting material **1**[10] and show two bands with medium intensities between 286 and 410 nm, while the UV−vis spectra of **2**, **3,** and **5** exhibit only a single absorption at 362−376 nm. As anticipated for these types of charge-transfer bands, the extinction coefficient of the ferrous compound is less than that of the ferric species.

The rhombic EPR spectra of the compounds **2**−**4**, measured with an X-band EPR spectrometer at 10 K in acetonitrile glass, are shown in Figure 1. Effective g values are collected in Table 6, and the designations are indicated in Figure 1. Tentative assignments have been made using the assumption that $D > h\nu$, where D is the axial zero field splitting parameter and $h\nu$ is the microwave photon energy. In this case the method of Hagen can be applied.[14] The complexes with two and three nitrito ligands, **3** and **4**, have relatively high g_y values and uniform line widths for the three observed bands; no other bands are observed with more extreme fields or at lower temperatures. These spin systems have similar rhombicity, and the best match of the observed peaks with those predicted for this type of low field experiment[14] is that they correspond to the three bands of the subspectrum arising from the Kramer's doublet with $E/D \sim 0.075$. These types of near axial systems often exhibit the $|\pm{}^1/_2\rangle$ subspectrum only.[14] On the other hand, the mono(nitrito) complex **2** exhibits more bands, some of which differ markedly in line width. In the temperature range studied, 4.2−45 K, the

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(12) (a) Richter-Addo, G. B.; Legzins, P. *Chem. Rev.* **1988**, *88*, 991. (b) Richter-Addo, G. B.; Legzins, P. *Metal Nitrosyls*; Oxford University Press: Oxford, U.K., 1992. (c) Bottomley, F. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1989; Vol. 2. (d) Bhattacharyya, R. G.; Mallik, M.; Ghosh, P. N. *Inorg. Chim. Acta* **1990**, *168*, 141.

(13) Bazulomslo, D. A.; Hollocher, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 7982.

(14) Hagen, W. R. *Adv. Inorg. Chem.* **1992**, *38*, 165.

Table 6. Summary of Physical Data for **2**−**6**

compd	IR (cm^{-1})^a			EPR (G)^b			UV−vis (nm)^c	
	ν_{asym}	ν_{sym}	δ	g_x	g_y	g_z	λ (ϵ)	$E_{1/2}$ (V)^d
2	1448	1017	809	4.20	4.20	5.20	376 (5490)	− 0.700
2($^{15}NO_2^-$)	1420	987	783					
3	1450	980	801	4.27	7.60	2.00	362 (6240)	−0.780
4	1464	980	800	4.28	7.50	1.98	358 (3880), 300 (4270)	−0.700
5	1484	998	805				378 (1490)	−0.610, +0.875^e
6	1476	1280					410 (4660), 286 (3570)	

^{a} Nitrite bands for samples measured as a KBr pellet. ^{b} Spectra measured at 10 K in acetonitrile glass. In addition to the bands assigned for **2**, the spectrum in Figure 1 has bands g_1 and g_2 at 9.91 and 4.03. ^{c} Measured in acetonitrile solution; ϵ in M^{-1} cm^{-1}. ^{d} E_p potentials in mV vs Ag/Ag$^+$ for irreversible couples in acetonitrile solution with 0.1 M NBu_4PF_6 as supporting electrolyte on a platinum-button working electrode. ^{e} $E_{1/2}$ for quasireversible oxidation.

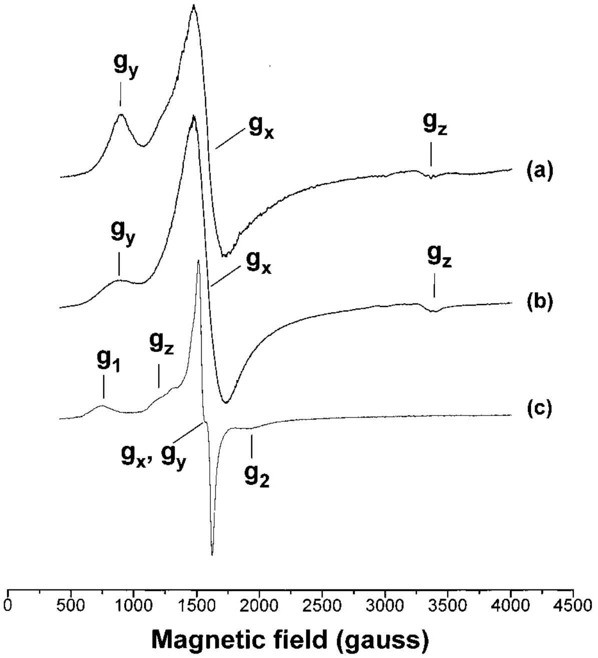
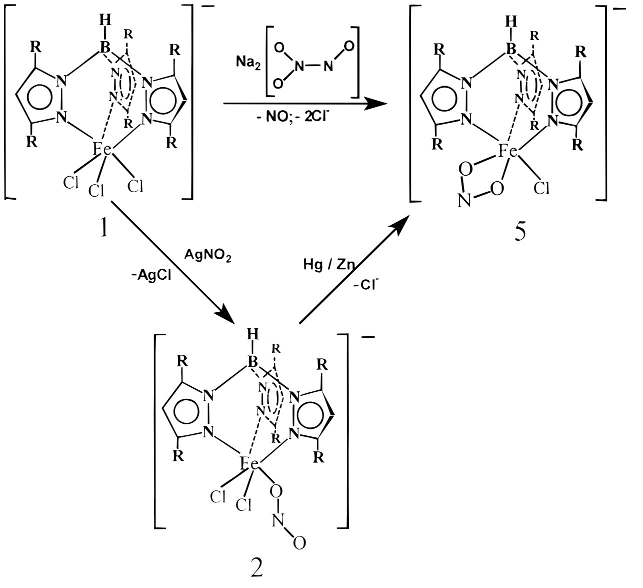


Figure 1. X-band EPR spectra of new ferric nitrite complexes: (a) **4**; (b) **3**; (c) **2**. Conditions: acetonitrile glass, 10 K, microwave frequency 9.565 614 GHz, receiver gain 2.5 × 10^4.

Scheme 1. Reaction Chemistry of **1** and **2**



EPR spectra of **2** did not exhibit bands lower than $g = 4$. In this case, we assign the intense relatively sharp slightly offset sigmoidal central band to an overlap of the g_x and g_y bands due to the $|\pm^3/_2\rangle$ subspectrum which would then place g_z at 5.1. Thus the iron environment has a higher rhombicity in **2** than in **3** or **4** with $E/D = 0.175$. In this assignment, the other peaks labeled g_1 and g_2 in Figure 1 at 9.91 and 4.03 are due to the other subspectra.

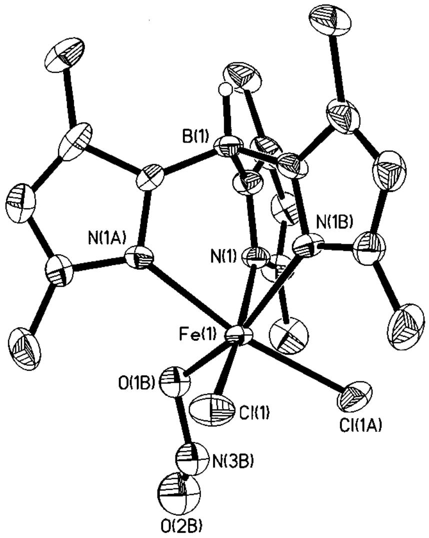


Figure 2. Molecular structure of the anion of **2**. Only one orientation of the disordered Cl and NO_2^- groups is shown, and hydrogen atoms are omitted for clarity.

The electrochemistries of the complexes **2**−**4** were surveyed by cyclic voltammetry and square-wave voltammetry. As listed in Table 6, all three compounds display only irreversible reduction between −700 and −780 mV in the cyclic voltammograms measured at 250 mv s^{-1}, with reductive decomposition leading to the formation of insoluble products. The ferrous nitrite complex **5** also has an irreversible reduction at −610 mV, but it also has a quasireversible oxidation at +735 mV which has $i_a/i_c = 0.87$. These observations support the assigned oxidation state in **5** with the relatively high oxidation potential being due in part to the stabilizing influence of the tris(pyrazolyl)borate ligand.

Solid State Crystal Structures of 2, 4, and 5. The solid-state structures of **2**, **4**, and **5** have been determined by X-ray crystallography to confirm their spectroscopically assigned structures. Only a few structures of iron−nitrite complexes have been reported, and the coordination mode of the nitrite ligands could not be unambiguously assigned on the basis of analytical and spectroscopic data. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Table 2, and perspective views of the three anionic complexes are presented in Figures 2−4.

The complex $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)Cl_2]$ (**2**) crystallizes in the polar space group $R3$. The iron center exhibits

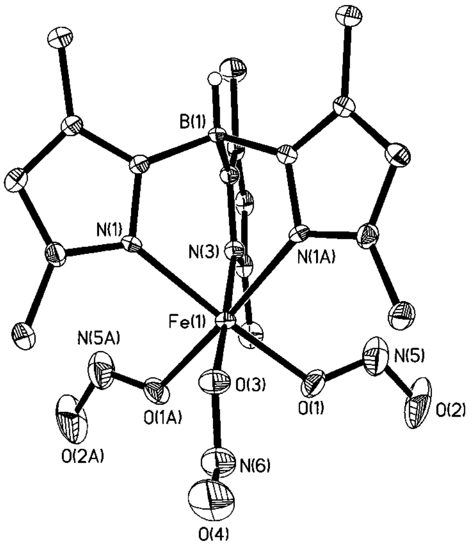


Figure 3. Molecular structure of the anion of **4**. Thermal ellipsoids are shown at the 20% probability level, and hydrogen atoms are omitted for clarity.

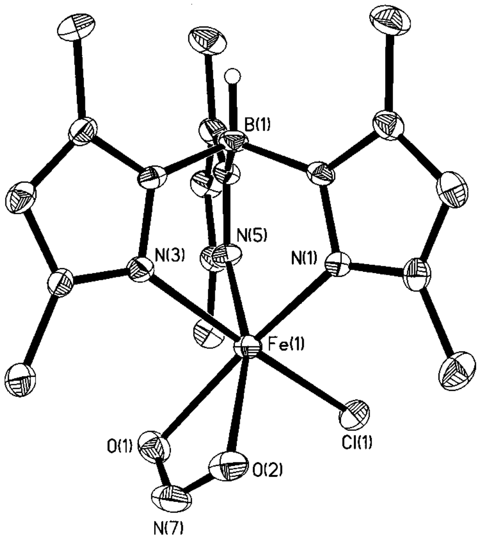


Figure 4. Molecular structure of the anion of **5**. Thermal ellipsoids are shown at the 20% probability level, and hydrogen atoms are omitted for clarity.

approximate octahedral geometry, coordinated by the tridentate pyrazolylborate ligand, two chloride ligands, and an O-bound nitrito group. The two chlorides and the atoms of the nitrite unit are disordered over three positions with respect to the C_3 axis formed by the iron and boron atoms. As a consequence, bond lengths, especially for the nitrite ligand, are not very accurate.

In contrast, the X-ray diffraction structures of $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(ONO)_3]$ (**4**) and $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(\eta^2\text{-}ONO)Cl]$ (**5**) are not disordered and the nitrite ligands in these two complexes adopt a single geometry. Complex **4** contains three O-bound nitrito ligands which adopt a very typical geometry in terms of average bond length [Fe−O 1.988(8) Å, N−O 1.12(2)−1.293 (11) Å] and bond angle [O−N−O 114.2(10)−118(2)°]. The bond parameters of the pyrazolylborate ligand [Fe−N 2.134(4)−2137(8) Å] are almost identical with those found in $[NEt_4][HB(pz)_3FeCl_3]$ and in $[NEt_4][HB(3,5\text{-}Me_2pz)_3Fe(N_3)_3]$.[10]

While the molecular structures of **2** and **4** exhibit monodentate nitrito coordination to ferric centers, the anion in **5** consists of a ferrous iron ligated by a chelating nitrito ligand. The octahedral coordination environment in **5** is completed by a chloride ligand and the pyrazolylborate unit. The change in nitrite coordination however has only a small effect with respect to the N−O bond lengths [1.258(10)−1.270(10) Å] and bond angle [113.2(8)°]. The major differences between **5** and **2**/**4** are elongation of the iron−oxygen bonds by about 0.2 Å, and the iron−nitrogen bond in **5** that is trans to the chlorine is 2.296(6) Å, substantially longer than the other iron−nitrogen bonds, which range from 2.098(6) to 2.134(5) Å in **5** and **4**.

Conclusions. The novel ferric nitrito complexes **2**−**4** and ferrous nitrite complex **5** have been prepared in facile, high-yield syntheses. Preferential O-bound nitrito coordination for the ferric compounds and chelating nitrite ligation for the ferrous iron complex have been demonstrated; no N-coordinated nitrite ligands have been observed in these systems. This may be attributed to possible steric interactions between the two oxygen atoms of an N-bound nitro group and the three methyl units in the pocket formed by the $[HB(3,5\text{-}Me_2pz)_3]$ ligand. In this regard, it may be significant that two crystallographically characterized $LCu(NO_2)$ complexes also contained chelated nitrito ligands, and this may well be the thermodynamically favored coordination mode for these ligands.[5b] What is especially surprising is that these compounds have been so difficult to transform into the corresponding nitrosyl complexes, especially in light of their facile preparation by direct nitrosylation of $[NEt_4][HB(3,5\text{-}Me_2pz)_3FeCl_3]$ (**1**) with nitric oxide.[15] To determine the origin of the implicit kinetic barriers that operate in this system, we are exploring the solution dynamic properties of nitrite exchange and ligand fluctionality in these unusual ferric nitrite complexes, and these results will be described in subsequent papers.

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Supporting Information Available: Tables of X-ray experimental details, bonds distances and angles, thermal parameters, and hydrogen coordinates and fully labeled ORTEP diagrams (17 pages). Ordering information is given on any current masthead page.

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