

## **(*N*-C<sub>n</sub>H<sub>2n-1</sub>)-1, 3-Azapropanedithiolate (n = 5, 6, 7) bridged diiron complexes as mimics for the active site of [FeFe]-hydrogenases: The influence of the bridge on diiron complex**

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Table 1. Selected bond lengths [Å] and angles [°] in **1**

N(1)-C(9)	1.349(6)	S(2)-Fe(1)-S(1)	84.28(4)
N(1)-C(7)	1.440(5)	S(2)-Fe(1)-Fe(2)	56.20(3)
N(1)-C(8)	1.441(5)	S(1)-Fe(1)-Fe(2)	56.16(3)
Fe(2)-S(2)	2.2512(10)	S(2)-Fe(2)-S(1)	84.54(3)
Fe(2)-S(1)	2.2523(10)	S(2)-Fe(2)-Fe(1)	56.31(3)
S(2)-C(8)	1.833(4)	S(1)-Fe(2)-Fe(1)	56.48(3)
S(1)-C(7)	1.841(4)	Fe(2)-S(2)-Fe(1)	67.49(3)
Fe(1)-S(2)	2.2541(10)	C(9)-N(1)-C(7)	119.1(4)
Fe(1)-S(1)	2.2606(10)	C(9)-N(1)-C(8)	119.9(4)
Fe(1)-Fe(2)	2.5025(7)	C(7)-N(1)-C(8)	110.7(3)

Table 2. Selected bond lengths [Å] and angles [°] in **2**

Fe(1)-S(1)	2.2441(15)	S(1)-Fe(1)-S(2)	84.70(5)
Fe(1)-S(2)	2.2528(14)	C(8)-N(1)-C(7)	112.7(5)
Fe(1)-Fe(2)	2.5280(10)	C(8)-N(1)-C(9)	112.7(5)
Fe(2)-S(2)	2.2393(14)	C(7)-N(1)-C(9)	115.5(5)
Fe(2)-S(1)	2.2511(15)	S(2)-Fe(2)-S(1)	84.85(5)
N(1)-C(7)	1.448(8)	S(2)-Fe(2)-Fe(1)	56.00(4)
N(1)-C(9)	1.491(7)	S(1)-Fe(2)-Fe(1)	55.65(4)
S(2)-C(8)	1.823(6)	Fe(1)-S(1)-Fe(2)	68.44(4)
S(1)-C(7)	1.845(6)	S(1)-Fe(1)-Fe(2)	55.91(4)
N(1)-C(8)	1.434(8)	S(2)-Fe(1)-Fe(2)	55.50(4)

Table 3. Selected bond lengths [Å] and angles [°] in **3**

Fe(1)-S(2)	2.2495(8)	S(2)-Fe(1)-Fe(2)	56.21(2)
Fe(1)-S(1)	2.2569(8)	S(1)-Fe(1)-Fe(2)	56.18(2)
Fe(1)-Fe(2)	2.5103(7)	S(2)-Fe(2)-S(1)	84.67(3)
N(1)-C(7)	1.435(3)	S(2)-Fe(2)-Fe(1)	56.04(2)
N(1)-C(8)	1.438(3)	S(1)-Fe(2)-Fe(1)	56.22(2)
S(2)-C(8)	1.840(3)	Fe(1)-S(2)-Fe(2)	67.75(2)
S(1)-C(7)	1.840(2)	Fe(2)-S(1)-Fe(1)	67.60(2)
Fe(2)-S(2)	2.2542(8)	C(7)-N(1)-C(8)	111.1(2)
Fe(2)-S(1)	2.2558(8)	C(7)-N(1)-C(9)	113.63(18)
S(2)-Fe(1)-S(1)	84.75(3)	C(8)-N(1)-C(9)	117.34(19)

Table 4. Selected bond lengths [Å] and angles [°] in **4**

C(11)-N(1)	1.449(10)	P(1)-Fe(1)-Fe(2)	153.52(8)
Fe(2)-P(2)	2.229(2)	S(2)-Fe(1)-Fe(2)	55.88(5)
Fe(2)-S(2)	2.2560(19)	S(1)-Fe(1)-Fe(2)	55.96(5)
Fe(2)-S(1)	2.262(2)	P(2)-Fe(2)-S(2)	92.78(8)
C(12)-S(1)	1.846(8)	P(2)-Fe(2)-S(1)	158.37(8)
S(2)-C(11)	1.826(7)	S(2)-Fe(2)-S(1)	83.99(7)
N(1)-C(13)	1.477(9)	P(2)-Fe(2)-Fe(1)	104.48(7)
Fe(1)-P(1)	2.224(2)	C(12)-N(1)-C(11)	111.4(6)
Fe(1)-S(2)	2.260(2)	C(12)-N(1)-C(13)	113.7(6)
Fe(1)-S(1)	2.270(2)	C(11)-N(1)-C(13)	111.9(6)
Fe(1)-Fe(2)	2.5279(13)	Fe(2)-S(2)-Fe(1)	68.08(6)
P(1)-Fe(1)-S(1)	102.20(8)	S(2)-Fe(2)-Fe(1)	56.04(6)
S(2)-Fe(1)-S(1)	83.72(7)	S(1)-Fe(2)-Fe(1)	56.25(6)

Table 5. Selected bond lengths [Å] and angles [°] in **5**

Fe(1)-P(1)	2.2276(12)	S(2)-Fe(1)-S(1)	84.42(4)
Fe(1)-S(2)	2.2410(11)	P(1)-Fe(1)-Fe(2)	113.97(4)
Fe(1)-S(1)	2.2536(11)	S(2)-Fe(1)-Fe(2)	54.30(3)
Fe(1)-Fe(2)	2.6374(8)	S(1)-Fe(1)-Fe(2)	53.64(3)
Fe(2)-P(2)	2.2329(12)	P(2)-Fe(2)-S(1)	87.31(4)
Fe(2)-S(1)	2.2334(11)	P(2)-Fe(2)-S(2)	169.32(4)
Fe(2)-S(2)	2.2540(11)	S(1)-Fe(2)-S(2)	84.59(4)
S(1)-C(12)	1.830(4)	P(2)-Fe(2)-Fe(1)	115.57(4)
S(2)-C(11)	1.834(4)	S(1)-Fe(2)-Fe(1)	54.36(3)
N(1)-C(12)	1.443(4)	S(2)-Fe(2)-Fe(1)	53.84(3)
N(1)-C(11)	1.447(4)	Fe(1)-S(2)-Fe(2)	71.85(3)
N(1)-C(13)	1.485(4)	C(12)-N(1)-C(11)	112.7(3)
P(1)-Fe(1)-S(2)	88.58(4)	C(12)-N(1)-C(13)	113.5(3)
P(1)-Fe(1)-S(1)	167.53(4)	C(11)-N(1)-C(13)	111.6(3)

Table 6. Selected bond lengths [Å] and angles [°] in **6**

Fe(2)-P(2)	2.2218(8)	P(1)-Fe(1)-S(1)	88.17(3)
Fe(2)-Fe(1)	2.612	P(1)-Fe(1)-S(2)	164.09(3)
Fe(2)-S(2)	2.2495(6)	S(1)-Fe(1)-S(2)	84.36(2)
N(1)-C(12)	1.443(3)	P(2)-Fe(2)-S(1)	164.28(3)
N(1)-C(11)	1.449(3)	P(2)-Fe(2)-S(2)	91.03(3)
N(1)-C(13)	1.490(3)	S(1)-Fe(2)-S(2)	84.27(2)
S(2)-C(12)	1.840(2)	Fe(1)-S(2)-Fe(2)	71.01(2)
S(1)-C(11)	1.833(2)	Fe(1)-S(1)-Fe(2)	71.11(2)
Fe(1)-P(1)	2.2259(8)	C(12)-N(1)-C(11)	112.27(19)
Fe(1)-S(1)	2.2447(6)	C(12)-N(1)-C(13)	114.50(19)
Fe(1)-S(2)	2.2476(7)	C(11)-N(1)-C(13)	112.36(18)