Electronic Supplementary Material (ESI) for Dalton Transactions.

The influence of metal-complexing macrocycle size on intramolecular movement in rotaxanes

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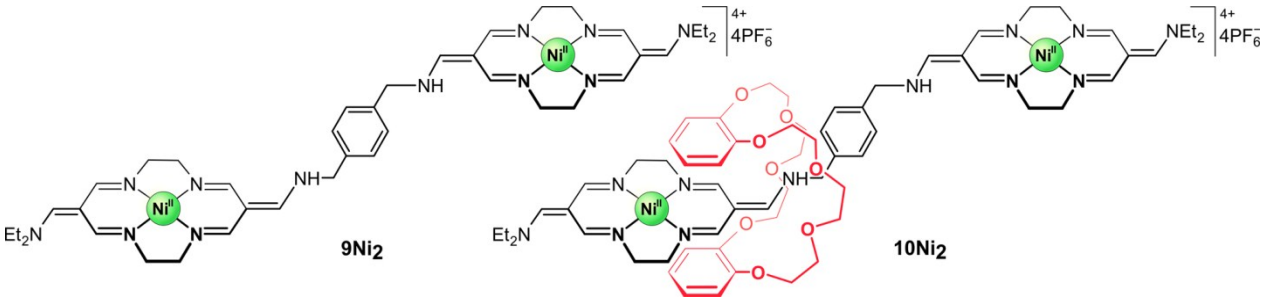


Scheme 1S. Structures of the axle **9Ni$_2$** and the [2]rotaxanes **10Ni$_2$**.

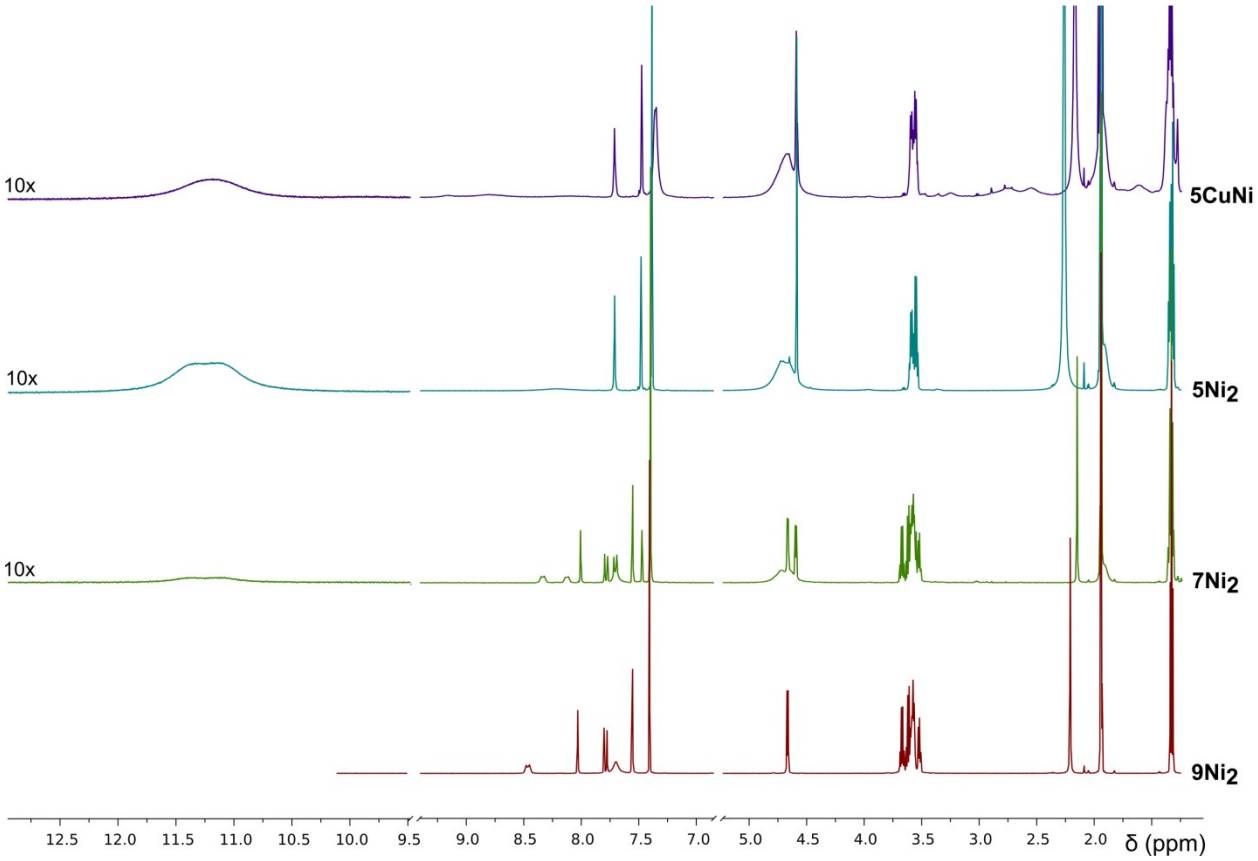


Figure 1S. 600 MHz ^{1}H NMR spectra of studied free axles in CD_3CN solution.

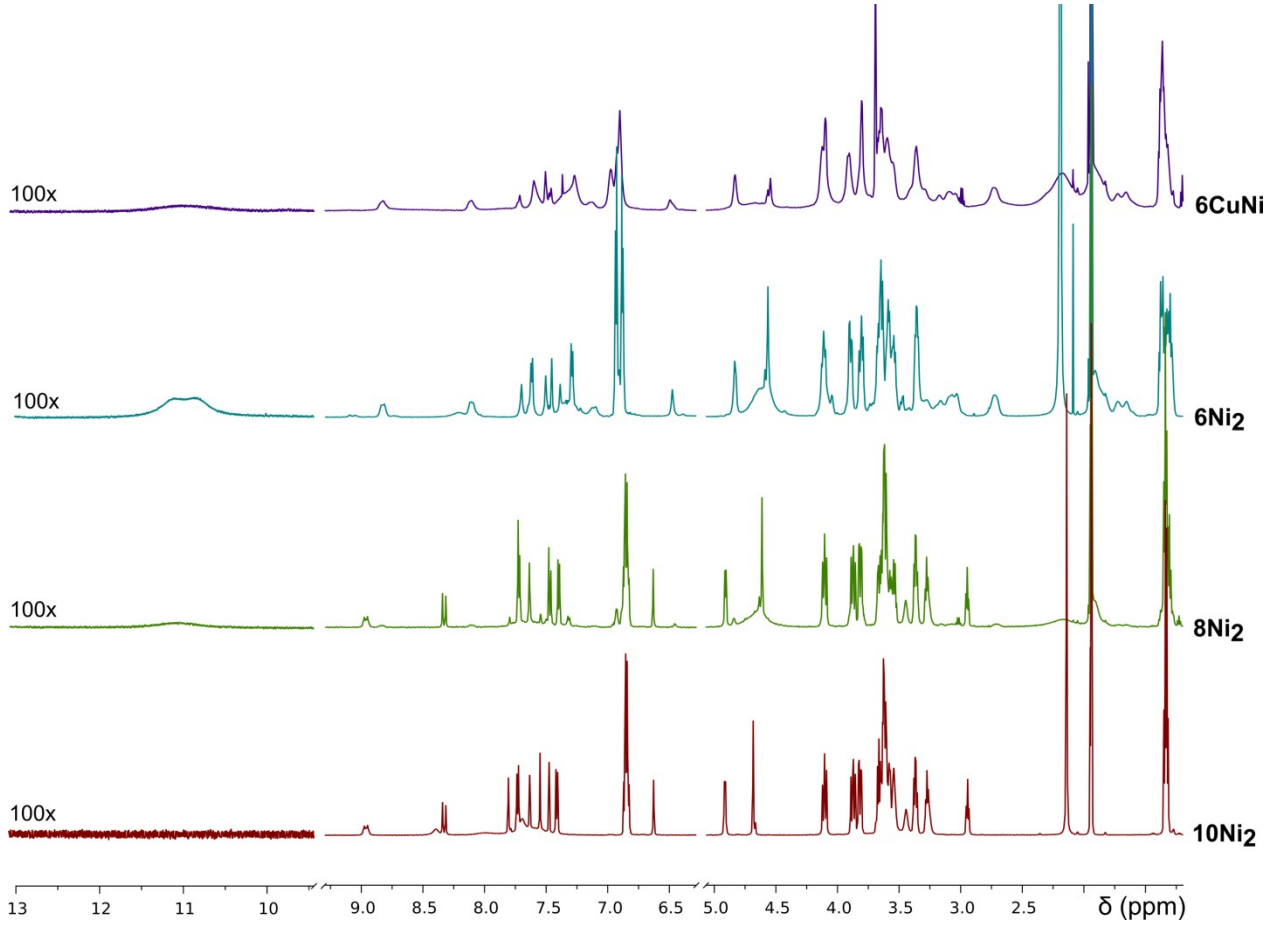


Figure 2S. 600 MHz ^{1}H NMR spectra of studied [2]rotaxanes in CD_3CN solution.

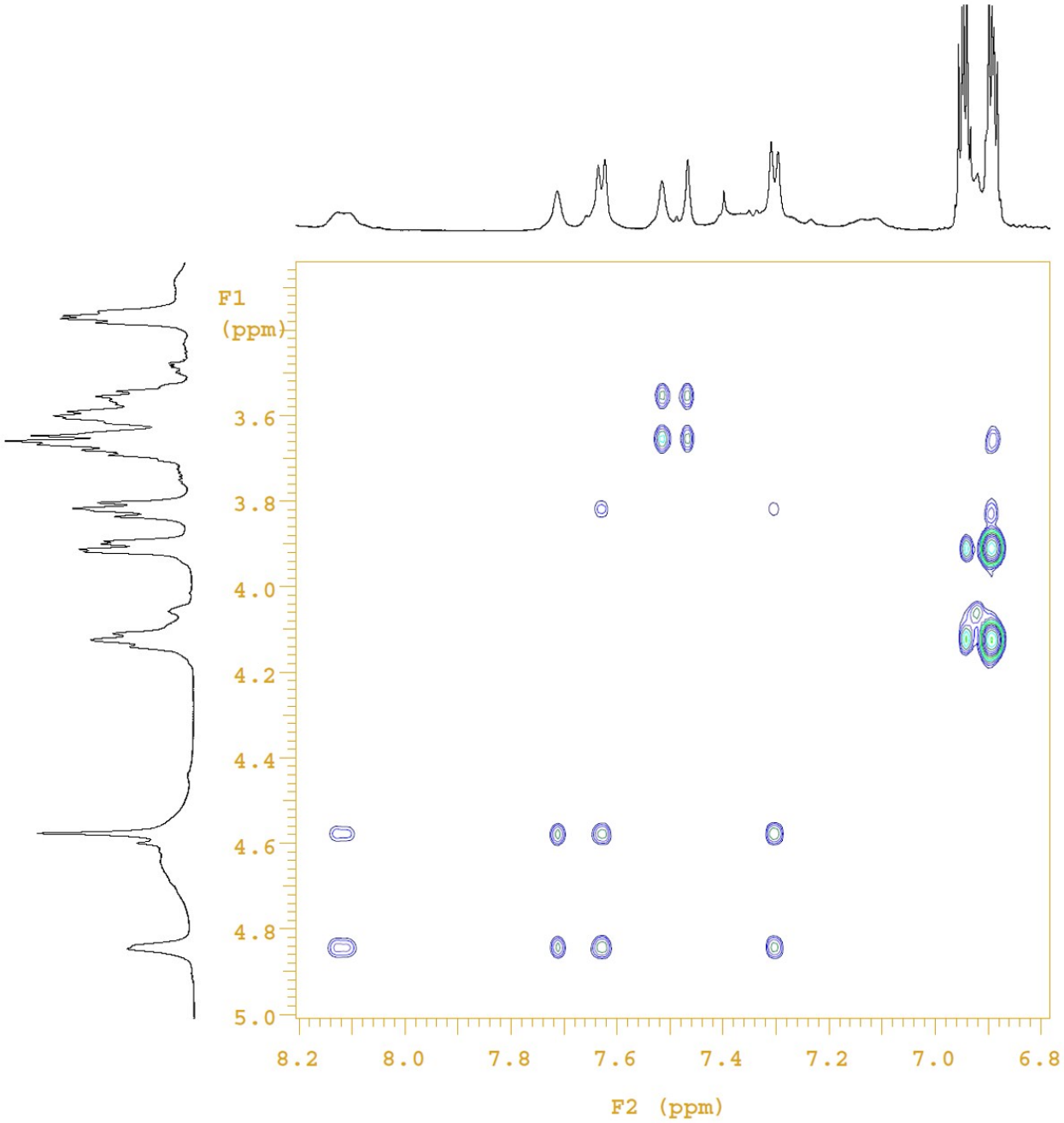
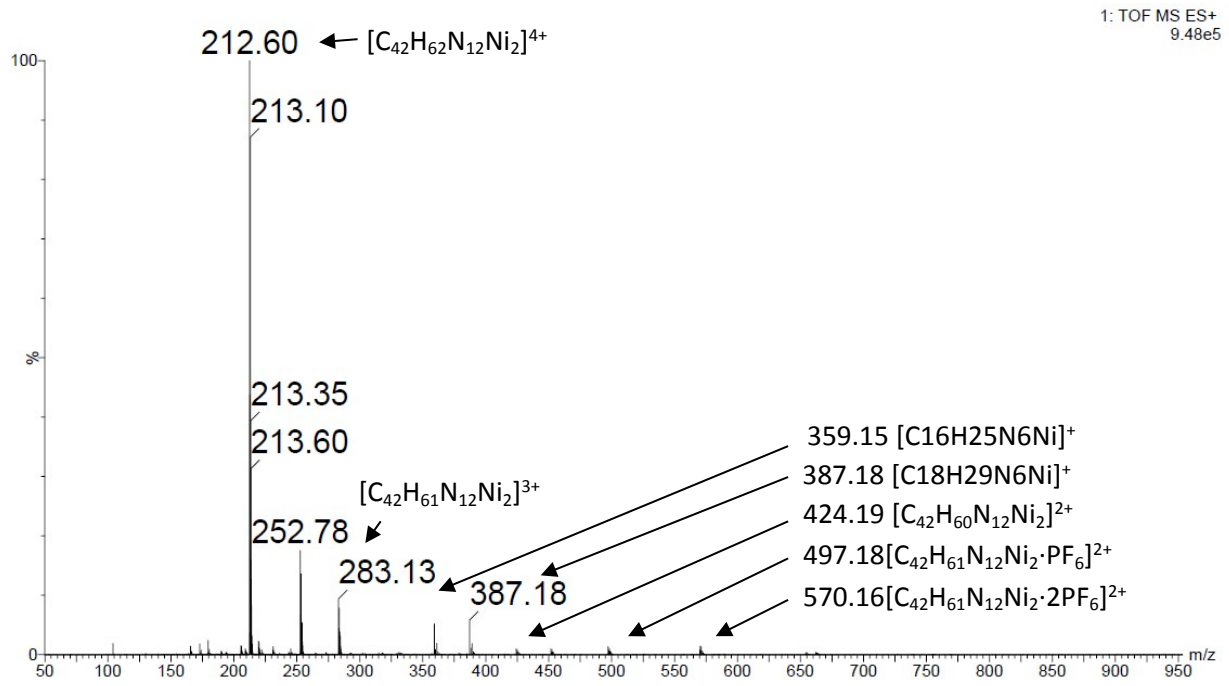


Figure 3S. Fragment of ^{1}H–^{1}H ROESY spectrum of rotaxane **6Ni$_2$** (600 MHz, CD_3CN).

(A)



(B)

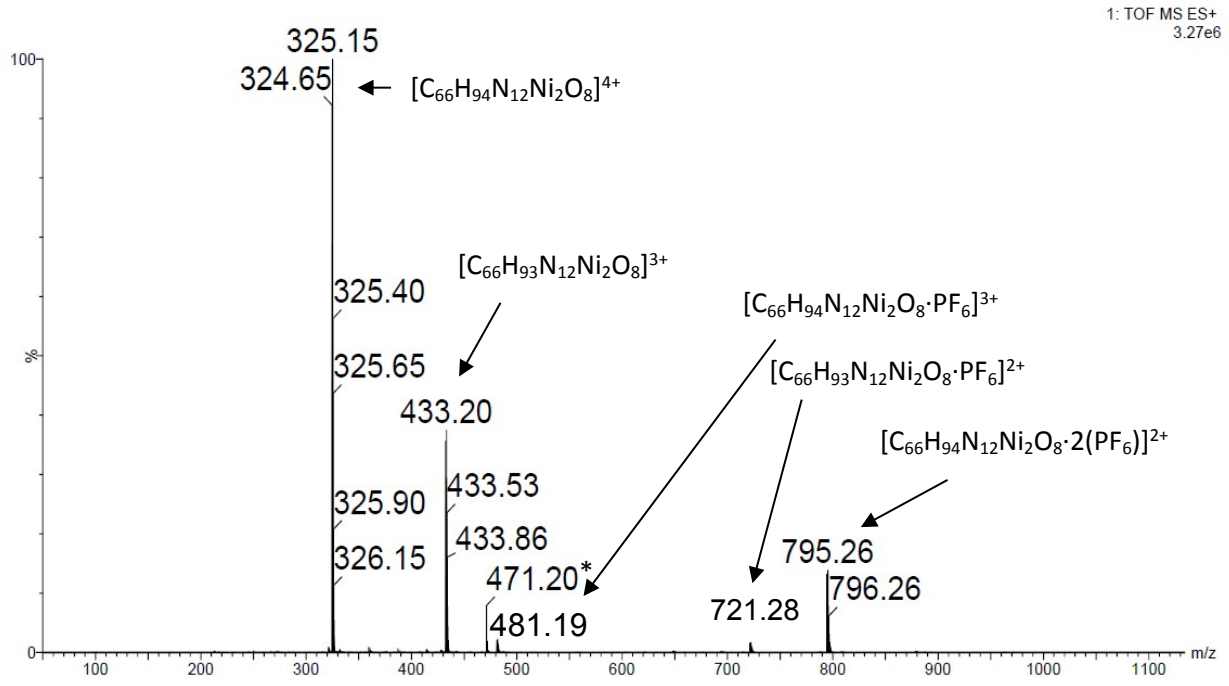


Figure 4S. ESI mass spectra of (A) axle **7Ni$_2$** and (B) [2]rotaxanes **8Ni$_2$** (* $[DB24C8Na]^+$).

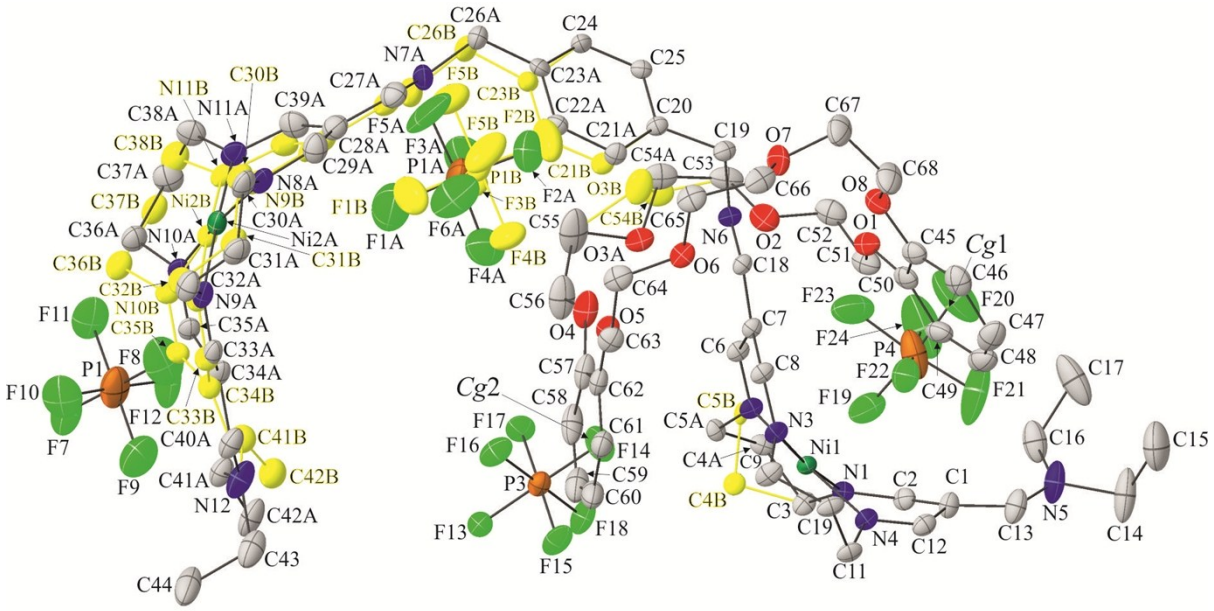


Figure 5S. Asymmetric unit of the crystal lattice of **6Ni$_2$**. Displacement ellipsoids are drawn at the 25% probability level. Hydrogen atoms were omitted for clarity. Minor parts of the disordered fragments are coloured in yellow. The *Cg*1 and *Cg*2 denote the geometric centers of gravity of the aromatic rings delineated by the C45−C50 and C57−C62 atoms, respectively.

Table 1S. Crystal data and structure refinement details for **6Ni$_2$**.

Identification code	**6Ni$_2$**
Empirical formula	$C_{68}H_{98}F_{24}N_{12}Ni_2O_8P_4$
Formula weight	1908.88
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9923(3)
b/Å	35.5936(14)
c/Å	22.7942(7)
α/°	90
β/°	94.338(3)
γ/°	90
Volume/Å^3	8083.8(5)
Z	4
ρ_{calc}g/cm^3	1.568
μ/mm^{-1}	2.359
F(000)	3944.0
Crystal size/mm^3	0.15 × 0.07 × 0.04
Radiation	Cu$K\alpha$ (λ = 1.54184)
2Θ range for data collection/°	4.612 to 134.158
Index ranges	-11 ≤ h ≤ 11, -40 ≤ k ≤ 42, -27 ≤ l ≤ 18
Reflections collected	33183
Independent reflections	14380 [R_{int} = 0.0546, R_{sigma} = 0.0819]
Data/restraints/parameters	14380/792/1319
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0900, wR_2 = 0.2484
Final R indexes [all data]	R_1 = 0.1444, wR_2 = 0.2973
Largest diff. peak/hole / e Å^{-3}	2.15/-0.74

Table 2S. The values of bond lengths in **6Ni$_2$**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(1)	C(2)	1.413(9)	C(39A)	N(11A)	1.40(2)
C(1)	C(12)	1.433(9)	C(40)	N(12)	1.298(10)
C(1)	C(13)	1.400(10)	C(41A)	C(42A)	1.49(3)
C(2)	N(1)	1.303(8)	C(41A)	N(12)	1.445(18)
C(3)	C(4A)	1.550(10)	C(41B)	C(42B)	1.43(3)
C(3)	C(4B)	1.53(3)	C(41B)	N(12)	1.59(2)
C(3)	N(1)	1.481(7)	C(43)	C(44)	1.547(16)
C(4A)	C(5A)	1.491(13)	C(43)	N(12)	1.495(13)
C(4B)	C(5B)	1.50(4)	F(19)	P(4)	1.571(7)
C(5A)	N(2)	1.514(8)	F(20)	P(4)	1.612(8)
C(5B)	N(2)	1.51(2)	F(21)	P(4)	1.512(7)
C(6)	C(7)	1.426(7)	F(22)	P(4)	1.556(5)
C(6)	N(2)	1.293(7)	F(23)	P(4)	1.601(8)
C(7)	C(8)	1.401(7)	F(24)	P(4)	1.563(8)
C(7)	C(18)	1.397(7)	N(1)	Ni(1)	1.906(5)
C(8)	N(3)	1.290(7)	N(2)	Ni(1)	1.891(5)
C(9)	C(10)	1.503(9)	N(3)	Ni(1)	1.905(5)
C(9)	N(3)	1.490(7)	N(4)	Ni(1)	1.910(5)
C(10)	C(11)	1.491(8)	N(8A)	Ni(2A)	1.911(15)
C(11)	N(4)	1.478(7)	N(9A)	Ni(2A)	1.883(11)
C(12)	N(4)	1.279(8)	N(10A)	Ni(2A)	1.882(13)
C(13)	N(5)	1.293(11)	N(11A)	Ni(2A)	1.900(11)
C(14)	C(15)	1.613(18)	C(45)	C(46)	1.379(11)
C(14)	N(5)	1.505(11)	C(45)	C(50)	1.413(10)
C(16)	C(17)	1.525(15)	C(45)	O(8)	1.356(8)
C(16)	N(5)	1.444(12)	C(46)	C(47)	1.420(13)
C(18)	N(6)	1.313(7)	C(47)	C(48)	1.345(14)
C(19)	C(20)	1.502(8)	C(48)	C(49)	1.378(13)
C(19)	N(6)	1.445(7)	C(49)	C(50)	1.379(10)
C(20)	C(21A)	1.404(13)	C(50)	O(1)	1.371(8)
C(20)	C(21B)	1.424(8)	C(51)	C(52)	1.493(11)
C(20)	C(25)	1.371(7)	C(51)	O(1)	1.434(8)
C(21A)	C(22A)	1.396(17)	C(52)	O(2)	1.417(10)
C(21B)	C(22B)	1.3151	C(53)	C(54A)	1.49(2)
C(22B)	C(23B)	1.3089	C(53)	C(54B)	1.48(3)
C(23B)	C(26B)	1.4736	C(53)	O(2)	1.437(8)
C(23B)	C(24)	1.432(7)	C(54A)	O(3A)	1.43(2)
C(26B)	N(7B)	1.4841	C(54B)	O(3B)	1.37(3)
C(27B)	C(28B)	1.5532	C(55)	C(56)	1.440(16)
C(27B)	N(7B)	1.2465	C(55)	O(3A)	1.505(13)
C(28B)	C(29B)	1.3735	C(55)	O(3B)	1.66(2)
C(28B)	C(39B)	1.3536	C(56)	O(4)	1.453(9)
C(29B)	N(8B)	1.3294	C(57)	C(58)	1.402(13)
C(30B)	C(31B)	1.5250	C(57)	C(62)	1.406(10)
C(30B)	N(8B)	1.4881	C(57)	O(4)	1.369(10)
C(31B)	C(32B)	1.5345	C(58)	C(59)	1.363(14)

C(32B)	N(9B)	1.4995	C(59)	C(60)	1.334(14)
C(33B)	C(34B)	1.4223	C(60)	C(61)	1.389(11)
C(33B)	N(9B)	1.2818	C(61)	C(62)	1.386(10)
C(34B)	C(35B)	1.4504	C(62)	O(5)	1.367(8)
C(34B)	C(40)	1.276(9)	C(63)	C(64)	1.471(10)
C(35B)	N(10B)	1.2657	C(63)	O(5)	1.437(7)
C(36B)	C(37B)	1.6314	C(64)	O(6)	1.435(9)
C(36B)	N(10B)	1.5176	C(65)	C(66)	1.484(12)
C(37B)	C(38B)	1.3642	C(65)	O(6)	1.413(8)
C(38B)	N(11B)	1.4244	C(66)	O(7)	1.397(9)
C(39B)	N(11B)	1.4520	C(67)	C(68)	1.478(8)
N(8B)	Ni(2B)	1.9557	C(67)	O(7)	1.431(10)
N(9B)	Ni(2B)	1.8778	C(68)	O(8)	1.473(9)
N(10B)	Ni(2B)	1.8913	F(1A)	P(1A)	1.57(2)
N(11B)	Ni(2B)	1.8987	F(2A)	P(1A)	1.582(19)
C(22A)	C(23A)	1.422(17)	F(3A)	P(1A)	1.627(18)
C(23A)	C(24)	1.439(15)	F(4A)	P(1A)	1.607(16)
C(23A)	C(26A)	1.483(18)	F(5A)	P(1A)	1.499(17)
C(24)	C(25)	1.374(8)	F(6A)	P(1A)	1.583(17)
C(26A)	N(7A)	1.417(16)	P(1B)	F(1B)	1.5808
C(27A)	C(28A)	1.41(2)	P(1B)	F(2B)	1.5690
C(27A)	N(7A)	1.281(18)	P(1B)	F(3B)	1.5611
C(28A)	C(29A)	1.45(2)	P(1B)	F(4B)	1.5570
C(28A)	C(39A)	1.38(2)	P(1B)	F(5B)	1.5767
C(29A)	N(8A)	1.32(2)	P(1B)	F(6B)	1.5752
C(30A)	C(31A)	1.51(2)	F(7)	P(2)	1.559(7)
C(30A)	N(8A)	1.44(2)	F(8)	P(2)	1.570(8)
C(31A)	C(32A)	1.47(2)	F(9)	P(2)	1.567(8)
C(32A)	N(9A)	1.51(2)	F(10)	P(2)	1.577(7)
C(33A)	C(34A)	1.43(2)	F(11)	P(2)	1.568(7)
C(33A)	N(9A)	1.300(19)	F(12)	P(2)	1.578(7)
C(34A)	C(35A)	1.459(17)	F(13)	P(3)	1.596(5)
C(34A)	C(40)	1.489(18)	F(14)	P(3)	1.594(5)
C(35A)	N(10A)	1.276(17)	F(15)	P(3)	1.596(4)
C(36A)	C(37A)	1.6312(11)	F(16)	P(3)	1.576(4)
C(36A)	N(10A)	1.454(16)	F(17)	P(3)	1.602(4)
C(37A)	C(38A)	1.3642(11)	F(18)	P(3)	1.601(4)
C(38A)	N(11A)	1.396(18)			

Table 3S. The values of valence angles in **6Ni$_2$**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(2)	C(1)	C(12)	116.5(6)	C(40)	N(12)	C(43)	117.9(7)
C(13)	C(1)	C(2)	127.3(6)	C(41A)	N(12)	C(43)	107.6(13)
C(13)	C(1)	C(12)	115.0(6)	C(43)	N(12)	C(41B)	130.7(10)
N(1)	C(2)	C(1)	124.8(5)	N(1)	Ni(1)	N(4)	88.6(2)
N(1)	C(3)	C(4A)	111.1(5)	N(2)	Ni(1)	N(1)	90.9(2)
N(1)	C(3)	C(4B)	110.7(9)	N(2)	Ni(1)	N(3)	88.90(19)
C(5A)	C(4A)	C(3)	111.6(6)	N(2)	Ni(1)	N(4)	177.0(2)
C(5B)	C(4B)	C(3)	101.7(19)	N(3)	Ni(1)	N(1)	174.6(2)
C(4A)	C(5A)	N(2)	109.7(7)	N(3)	Ni(1)	N(4)	91.30(19)

C(4B)	C(5B)	N(2)	104(2)	N(9A)	Ni(2A)	N(8A)	90.8(7)
N(2)	C(6)	C(7)	124.1(5)	N(9A)	Ni(2A)	N(11A)	176.6(6)
C(8)	C(7)	C(6)	118.0(5)	N(10A)	Ni(2A)	N(8A)	175.1(5)
C(18)	C(7)	C(6)	122.2(5)	N(10A)	Ni(2A)	N(9A)	87.3(6)
C(18)	C(7)	C(8)	118.3(5)	N(10A)	Ni(2A)	N(11A)	90.7(5)
N(3)	C(8)	C(7)	125.6(5)	N(11A)	Ni(2A)	N(8A)	91.0(6)
N(3)	C(9)	C(10)	112.0(5)	F(19)	P(4)	F(20)	173.6(5)
C(11)	C(10)	C(9)	110.1(5)	F(19)	P(4)	F(23)	86.6(3)
N(4)	C(11)	C(10)	112.0(5)	F(21)	P(4)	F(19)	97.7(5)
N(4)	C(12)	C(1)	126.2(6)	F(21)	P(4)	F(20)	88.0(6)
N(5)	C(13)	C(1)	132.1(8)	F(21)	P(4)	F(22)	92.7(4)
N(5)	C(14)	C(15)	108.7(10)	F(21)	P(4)	F(23)	174.8(6)
N(5)	C(16)	C(17)	111.3(9)	F(21)	P(4)	F(24)	90.8(5)
N(6)	C(18)	C(7)	126.5(5)	F(22)	P(4)	F(19)	91.0(3)
N(6)	C(19)	C(20)	114.3(5)	F(22)	P(4)	F(20)	85.9(4)
C(21A)	C(20)	C(19)	117.2(7)	F(22)	P(4)	F(23)	90.0(4)
C(21B)	C(20)	C(19)	124.6(5)	F(22)	P(4)	F(24)	174.5(6)
C(25)	C(20)	C(19)	121.1(5)	F(23)	P(4)	F(20)	87.8(5)
C(25)	C(20)	C(21A)	119.8(7)	F(24)	P(4)	F(19)	92.8(4)
C(25)	C(20)	C(21B)	112.4(6)	F(24)	P(4)	F(20)	90.0(5)
C(22A)	C(21A)	C(20)	120.0(10)	F(24)	P(4)	F(23)	86.2(5)
C(22B)	C(21B)	C(20)	121.3(4)	C(46)	C(45)	C(50)	119.8(7)
C(23B)	C(22B)	C(21B)	127.7	O(8)	C(45)	C(46)	124.8(7)
C(22B)	C(23B)	C(26B)	132.7	O(8)	C(45)	C(50)	115.4(6)
C(22B)	C(23B)	C(24)	112.6(4)	C(45)	C(46)	C(47)	118.8(8)
C(24)	C(23B)	C(26B)	114.6(4)	C(48)	C(47)	C(46)	121.1(9)
C(23B)	C(26B)	N(7B)	113.4	C(47)	C(48)	C(49)	119.9(9)
N(7B)	C(27B)	C(28B)	118.5	C(48)	C(49)	C(50)	121.3(9)
C(29B)	C(28B)	C(27B)	107.6	C(49)	C(50)	C(45)	118.9(7)
C(39B)	C(28B)	C(27B)	120.2	O(1)	C(50)	C(45)	116.5(6)
C(39B)	C(28B)	C(29B)	129.4	O(1)	C(50)	C(49)	124.5(7)
N(8B)	C(29B)	C(28B)	114.8	O(1)	C(51)	C(52)	108.4(6)
N(8B)	C(30B)	C(31B)	113.3	O(2)	C(52)	C(51)	109.7(6)
C(30B)	C(31B)	C(32B)	109.7	O(2)	C(53)	C(54A)	108.9(10)
N(9B)	C(32B)	C(31B)	113.0	O(2)	C(53)	C(54B)	111.0(15)
N(9B)	C(33B)	C(34B)	123.5	O(3A)	C(54A)	C(53)	109.2(15)
C(33B)	C(34B)	C(35B)	117.4	O(3B)	C(54B)	C(53)	111(2)
C(40)	C(34B)	C(33B)	117.5(6)	C(56)	C(55)	O(3A)	96.9(9)
C(40)	C(34B)	C(35B)	124.1(6)	C(56)	C(55)	O(3B)	132.3(9)
N(10B)	C(35B)	C(34B)	121.5	C(55)	C(56)	O(4)	107.5(9)
N(10B)	C(36B)	C(37B)	107.9	C(58)	C(57)	C(62)	119.3(9)
C(38B)	C(37B)	C(36B)	116.7	O(4)	C(57)	C(58)	125.1(8)
C(37B)	C(38B)	N(11B)	110.5	O(4)	C(57)	C(62)	115.5(7)
C(28B)	C(39B)	N(11B)	123.6	C(59)	C(58)	C(57)	120.9(8)
C(27B)	N(7B)	C(26B)	121.3	C(60)	C(59)	C(58)	119.6(9)
C(29B)	N(8B)	C(30B)	107.5	C(59)	C(60)	C(61)	122.0(10)
C(29B)	N(8B)	Ni(2B)	127.7	C(62)	C(61)	C(60)	120.0(8)
C(30B)	N(8B)	Ni(2B)	124.4	C(61)	C(62)	C(57)	118.0(8)
C(32B)	N(9B)	Ni(2B)	121.0	O(5)	C(62)	C(57)	116.2(7)

C(33B)	N(9B)	C(32B)	115.3	O(5)	C(62)	C(61)	125.8(6)
C(33B)	N(9B)	Ni(2B)	123.6	O(5)	C(63)	C(64)	109.9(5)
C(35B)	N(10B)	C(36B)	117.8	O(6)	C(64)	C(63)	110.7(6)
C(35B)	N(10B)	Ni(2B)	125.2	O(6)	C(65)	C(66)	110.9(6)
C(36B)	N(10B)	Ni(2B)	117.1	O(7)	C(66)	C(65)	109.5(6)
C(38B)	N(11B)	C(39B)	120.4	O(7)	C(67)	C(68)	110.7(7)
C(38B)	N(11B)	Ni(2B)	123.0	O(8)	C(68)	C(67)	107.6(7)
C(39B)	N(11B)	Ni(2B)	116.5	C(50)	O(1)	C(51)	117.3(5)
N(9B)	Ni(2B)	N(8B)	90.3	C(52)	O(2)	C(53)	112.6(6)
N(9B)	Ni(2B)	N(10B)	87.4	C(54A)	O(3A)	C(55)	104.2(11)
N(9B)	Ni(2B)	N(11B)	176.3	C(54B)	O(3B)	C(55)	98.2(17)
N(10B)	Ni(2B)	N(8B)	174.9	C(57)	O(4)	C(56)	115.9(8)
N(10B)	Ni(2B)	N(11B)	92.3	C(62)	O(5)	C(63)	115.0(5)
N(11B)	Ni(2B)	N(8B)	89.7	C(65)	O(6)	C(64)	111.6(5)
C(21A)	C(22A)	C(23A)	119.6(12)	C(66)	O(7)	C(67)	118.8(6)
C(22A)	C(23A)	C(24)	118.8(11)	C(45)	O(8)	C(68)	112.3(6)
C(22A)	C(23A)	C(26A)	117.9(12)	F(1A)	P(1A)	F(2A)	173.7(13)
C(24)	C(23A)	C(26A)	123.1(11)	F(1A)	P(1A)	F(3A)	89.3(12)
C(25)	C(24)	C(23B)	121.1(6)	F(1A)	P(1A)	F(4A)	84.5(10)
C(25)	C(24)	C(23A)	118.0(7)	F(1A)	P(1A)	F(6A)	93.7(11)
C(20)	C(25)	C(24)	122.0(6)	F(2A)	P(1A)	F(3A)	86.5(10)
N(7A)	C(26A)	C(23A)	118.0(11)	F(2A)	P(1A)	F(4A)	90.6(10)
N(7A)	C(27A)	C(28A)	123.4(15)	F(2A)	P(1A)	F(6A)	90.2(12)
C(27A)	C(28A)	C(29A)	112.7(14)	F(4A)	P(1A)	F(3A)	87.8(10)
C(39A)	C(28A)	C(27A)	121.9(15)	F(5A)	P(1A)	F(1A)	91.6(12)
C(39A)	C(28A)	C(29A)	123.2(15)	F(5A)	P(1A)	F(2A)	93.2(12)
N(8A)	C(29A)	C(28A)	119.9(15)	F(5A)	P(1A)	F(3A)	91.1(11)
N(8A)	C(30A)	C(31A)	113.9(15)	F(5A)	P(1A)	F(4A)	175.9(13)
C(32A)	C(31A)	C(30A)	110.4(15)	F(5A)	P(1A)	F(6A)	92.2(11)
C(31A)	C(32A)	N(9A)	114.7(15)	F(6A)	P(1A)	F(3A)	175.5(13)
N(9A)	C(33A)	C(34A)	125.5(13)	F(6A)	P(1A)	F(4A)	89.1(10)
C(33A)	C(34A)	C(35A)	112.1(13)	F(2B)	P(1B)	F(1B)	177.9
C(33A)	C(34A)	C(40)	114.0(12)	F(2B)	P(1B)	F(5B)	89.7
C(35A)	C(34A)	C(40)	129.6(15)	F(2B)	P(1B)	F(6B)	91.3
N(10A)	C(35A)	C(34A)	127.2(14)	F(3B)	P(1B)	F(1B)	90.9
N(10A)	C(36A)	C(37A)	110.6(11)	F(3B)	P(1B)	F(2B)	91.0
C(38A)	C(37A)	C(36A)	114.1(12)	F(3B)	P(1B)	F(5B)	90.1
C(37A)	C(38A)	N(11A)	117.0(14)	F(3B)	P(1B)	F(6B)	177.3
C(28A)	C(39A)	N(11A)	124.5(14)	F(4B)	P(1B)	F(1B)	89.1
C(34B)	C(40)	N(12)	131.0(8)	F(4B)	P(1B)	F(2B)	90.2
N(12)	C(40)	C(34A)	133.0(10)	F(4B)	P(1B)	F(3B)	88.6
N(12)	C(41A)	C(42A)	115.8(14)	F(4B)	P(1B)	F(5B)	178.7
C(42B)	C(41B)	N(12)	111.6(15)	F(4B)	P(1B)	F(6B)	92.8
N(12)	C(43)	C(44)	110.8(8)	F(5B)	P(1B)	F(1B)	91.0
C(2)	N(1)	C(3)	114.9(5)	F(6B)	P(1B)	F(1B)	86.7
C(2)	N(1)	Ni(1)	122.4(4)	F(6B)	P(1B)	F(5B)	88.6
C(3)	N(1)	Ni(1)	122.7(4)	F(7)	P(2)	F(8)	179.1(5)
C(5A)	N(2)	Ni(1)	119.9(4)	F(7)	P(2)	F(9)	92.3(5)
C(5B)	N(2)	Ni(1)	120.5(10)	F(7)	P(2)	F(10)	89.0(4)

C(6)	N(2)	C(5A)	115.8(5)	F(7)	P(2)	F(11)	88.4(4)
C(6)	N(2)	C(5B)	110.6(12)	F(7)	P(2)	F(12)	90.6(4)
C(6)	N(2)	Ni(1)	124.2(4)	F(8)	P(2)	F(10)	90.8(4)
C(8)	N(3)	C(9)	115.3(5)	F(8)	P(2)	F(12)	89.7(5)
C(8)	N(3)	Ni(1)	122.9(4)	F(9)	P(2)	F(8)	88.6(5)
C(9)	N(3)	Ni(1)	121.8(4)	F(9)	P(2)	F(10)	87.6(5)
C(11)	N(4)	Ni(1)	121.5(4)	F(9)	P(2)	F(11)	178.2(6)
C(12)	N(4)	C(11)	116.4(5)	F(9)	P(2)	F(12)	90.7(6)
C(12)	N(4)	Ni(1)	121.9(4)	F(10)	P(2)	F(12)	178.2(5)
C(13)	N(5)	C(14)	120.3(9)	F(11)	P(2)	F(8)	90.8(5)
C(13)	N(5)	C(16)	124.0(7)	F(11)	P(2)	F(10)	90.7(4)
C(16)	N(5)	C(14)	115.7(8)	F(11)	P(2)	F(12)	91.0(4)
C(18)	N(6)	C(19)	124.1(5)	F(13)	P(3)	F(17)	88.4(2)
C(27A)	N(7A)	C(26A)	125.2(13)	F(13)	P(3)	F(18)	88.7(3)
C(29A)	N(8A)	C(30A)	111.0(15)	F(14)	P(3)	F(13)	177.9(3)
C(29A)	N(8A)	Ni(2A)	125.0(13)	F(14)	P(3)	F(15)	90.3(3)
C(30A)	N(8A)	Ni(2A)	123.9(11)	F(14)	P(3)	F(17)	90.9(2)
C(32A)	N(9A)	Ni(2A)	120.4(11)	F(14)	P(3)	F(18)	89.3(3)
C(33A)	N(9A)	C(32A)	115.6(12)	F(15)	P(3)	F(13)	90.4(3)
C(33A)	N(9A)	Ni(2A)	123.4(11)	F(15)	P(3)	F(17)	178.5(3)
C(35A)	N(10A)	C(36A)	116.9(13)	F(15)	P(3)	F(18)	89.5(2)
C(35A)	N(10A)	Ni(2A)	122.6(9)	F(16)	P(3)	F(13)	90.8(3)
C(36A)	N(10A)	Ni(2A)	120.5(9)	F(16)	P(3)	F(14)	91.2(3)
C(38A)	N(11A)	C(39A)	117.4(12)	F(16)	P(3)	F(15)	90.5(2)
C(38A)	N(11A)	Ni(2A)	124.0(10)	F(16)	P(3)	F(17)	90.3(2)
C(39A)	N(11A)	Ni(2A)	118.6(10)	F(16)	P(3)	F(18)	179.5(3)
C(40)	N(12)	C(41A)	130.9(11)	F(18)	P(3)	F(17)	89.7(2)
C(40)	N(12)	C(41B)	111.2(11)				

Table 4S. The values of torsion angles in **6Ni$_2$**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C(1)	C(2)	N(1)	C(3)	-164.0(6)	C(26A)	C(23A)	C(24)	C(25)	171.2(10)
C(1)	C(2)	N(1)	Ni(1)	17.2(9)	C(27A)	C(28A)	C(29A)	N(8A)	-178.3(15)
C(1)	C(12)	N(4)	C(11)	170.4(6)	C(27A)	C(28A)	C(39A)	N(11A)	-177.4(15)
C(1)	C(12)	N(4)	Ni(1)	-15.0(9)	C(28A)	C(27A)	N(7A)	C(26A)	171.6(14)
C(1)	C(13)	N(5)	C(14)	-175.3(10)	C(28A)	C(29A)	N(8A)	C(30A)	-167.0(14)
C(1)	C(13)	N(5)	C(16)	4.8(17)	C(28A)	C(29A)	N(8A)	Ni(2A)	17(2)
C(2)	C(1)	C(12)	N(4)	-22.2(10)	C(28A)	C(39A)	N(11A)	C(38A)	162.8(15)
C(2)	C(1)	C(13)	N(5)	26.8(15)	C(28A)	C(39A)	N(11A)	Ni(2A)	-21(2)
C(3)	C(4A)	C(5A)	N(2)	66.7(8)	C(29A)	C(28A)	C(39A)	N(11A)	-15(3)
C(3)	C(4B)	C(5B)	N(2)	-89.1(19)	C(30A)	C(31A)	C(32A)	N(9A)	62(2)
C(4A)	C(3)	N(1)	C(2)	-124.0(6)	C(31A)	C(30A)	N(8A)	C(29A)	-122.3(16)
C(4A)	C(3)	N(1)	Ni(1)	54.9(7)	C(31A)	C(30A)	N(8A)	Ni(2A)	54.2(16)
C(4A)	C(5A)	N(2)	C(6)	119.3(7)	C(31A)	C(32A)	N(9A)	C(33A)	114.3(18)
C(4A)	C(5A)	N(2)	Ni(1)	-64.1(8)	C(31A)	C(32A)	N(9A)	Ni(2A)	-57.9(18)
C(4B)	C(3)	N(1)	C(2)	-171.4(11)	C(32A)	N(9A)	Ni(2A)	N(8A)	38.2(12)
C(4B)	C(3)	N(1)	Ni(1)	7.4(12)	C(32A)	N(9A)	Ni(2A)	N(10A)	-146.3(12)
C(4B)	C(5B)	N(2)	C(6)	-160.2(15)	C(33A)	C(34A)	C(35A)	N(10A)	24(2)
C(4B)	C(5B)	N(2)	Ni(1)	43(2)	C(33A)	C(34A)	C(40)	N(12)	-178.7(13)
C(5A)	N(2)	Ni(1)	N(1)	45.2(6)	C(33A)	N(9A)	Ni(2A)	N(8A)	-133.4(15)

C(5A)	N(2)	Ni(1)	N(3)	-140.2(6)	C(33A)	N(9A)	Ni(2A)	N(10A)	42.1(15)
C(5B)	N(2)	Ni(1)	N(1)	15.0(16)	C(34A)	C(33A)	N(9A)	C(32A)	171.2(17)
C(5B)	N(2)	Ni(1)	N(3)	-170.4(16)	C(34A)	C(33A)	N(9A)	Ni(2A)	-17(3)
C(6)	C(7)	C(8)	N(3)	18.5(9)	C(34A)	C(35A)	N(10A)	C(36A)	-164.4(15)
C(6)	C(7)	C(18)	N(6)	-11.4(9)	C(34A)	C(35A)	N(10A)	Ni(2A)	15(2)
C(6)	N(2)	Ni(1)	N(1)	-138.5(5)	C(34A)	C(40)	N(12)	C(41A)	-24(2)
C(6)	N(2)	Ni(1)	N(3)	36.1(5)	C(34A)	C(40)	N(12)	C(43)	179.9(13)
C(7)	C(6)	N(2)	C(5A)	162.0(7)	C(35A)	C(34A)	C(40)	N(12)	27(3)
C(7)	C(6)	N(2)	C(5B)	-170.2(14)	C(35A)	N(10A)	Ni(2A)	N(9A)	-41.0(11)
C(7)	C(6)	N(2)	Ni(1)	-14.4(8)	C(35A)	N(10A)	Ni(2A)	N(11A)	136.2(11)
C(7)	C(8)	N(3)	C(9)	-165.5(6)	C(36A)	C(37A)	C(38A)	N(11A)	55(2)
C(7)	C(8)	N(3)	Ni(1)	16.6(9)	C(36A)	N(10A)	Ni(2A)	N(9A)	138.7(10)
C(7)	C(18)	N(6)	C(19)	-175.7(5)	C(36A)	N(10A)	Ni(2A)	N(11A)	-44.1(10)
C(8)	C(7)	C(18)	N(6)	-177.4(6)	C(37A)	C(36A)	N(10A)	C(35A)	-123.6(14)
C(9)	C(10)	C(11)	N(4)	66.7(7)	C(37A)	C(36A)	N(10A)	Ni(2A)	56.7(15)
C(10)	C(9)	N(3)	C(8)	-121.5(6)	C(37A)	C(38A)	N(11A)	C(39A)	122.9(16)
C(10)	C(9)	N(3)	Ni(1)	56.5(7)	C(37A)	C(38A)	N(11A)	Ni(2A)	-53.2(18)
C(10)	C(11)	N(4)	C(12)	116.1(6)	C(38A)	N(11A)	Ni(2A)	N(8A)	-144.5(12)
C(10)	C(11)	N(4)	Ni(1)	-58.5(7)	C(38A)	N(11A)	Ni(2A)	N(10A)	40.0(12)
C(12)	C(1)	C(2)	N(1)	20.8(10)	C(39A)	C(28A)	C(29A)	N(8A)	18(3)
C(12)	C(1)	C(13)	N(5)	-166.1(9)	C(39A)	N(11A)	Ni(2A)	N(8A)	39.4(12)
C(13)	C(1)	C(2)	N(1)	-172.2(7)	C(39A)	N(11A)	Ni(2A)	N(10A)	-136.0(12)
C(13)	C(1)	C(12)	N(4)	169.3(7)	C(40)	C(34B)	C(35B)	N(10B)	-167.4(6)
C(15)	C(14)	N(5)	C(13)	-83.3(14)	C(40)	C(34A)	C(35A)	N(10A)	178.6(15)
C(15)	C(14)	N(5)	C(16)	96.6(11)	C(42A)	C(41A)	N(12)	C(40)	168.7(17)
C(17)	C(16)	N(5)	C(13)	128.6(11)	C(42A)	C(41A)	N(12)	C(43)	-34(2)
C(17)	C(16)	N(5)	C(14)	-51.3(13)	C(42B)	C(41B)	N(12)	C(40)	160.8(14)
C(18)	C(7)	C(8)	N(3)	-174.8(6)	C(42B)	C(41B)	N(12)	C(43)	-15(2)
C(19)	C(20)	C(21A)	C(22A)	167.9(7)	C(44)	C(43)	N(12)	C(40)	89.4(11)
C(19)	C(20)	C(21B)	C(22B)	-178.4(4)	C(44)	C(43)	N(12)	C(41A)	-71.6(13)
C(19)	C(20)	C(25)	C(24)	-175.2(5)	C(44)	C(43)	N(12)	C(41B)	-95.1(16)
C(20)	C(19)	N(6)	C(18)	-105.7(6)	N(1)	C(3)	C(4A)	C(5A)	-62.4(8)
C(20)	C(21A)	C(22A)	C(23A)	-1.2(13)	N(1)	C(3)	C(4B)	C(5B)	62.2(17)
C(20)	C(21B)	C(22B)	C(23B)	6.0(7)	N(2)	C(6)	C(7)	C(8)	-19.8(9)
C(21A)	C(20)	C(25)	C(24)	-11.3(9)	N(2)	C(6)	C(7)	C(18)	174.1(6)
C(21A)	C(22A)	C(23A)	C(24)	6.4(15)	N(3)	C(9)	C(10)	C(11)	-65.5(7)
C(21A)	C(22A)	C(23A)	C(26A)	-178.3(11)	N(6)	C(19)	C(20)	C(21A)	65.4(8)
C(21B)	C(20)	C(25)	C(24)	19.7(9)	N(6)	C(19)	C(20)	C(21B)	32.9(9)
C(21B)	C(22B)	C(23B)	C(26B)	-179.3	N(6)	C(19)	C(20)	C(25)	-130.3(5)
C(21B)	C(22B)	C(23B)	C(24)	-2.3(8)	N(7A)	C(27A)	C(28A)	C(29A)	173.7(15)
C(22B)	C(23B)	C(26B)	N(7B)	-14.8	N(7A)	C(27A)	C(28A)	C(39A)	-23(2)
C(22B)	C(23B)	C(24)	C(25)	7.7(10)	N(8A)	C(30A)	C(31A)	C(32A)	-60.0(18)
C(23B)	C(26B)	N(7B)	C(27B)	92.2	N(9A)	C(33A)	C(34A)	C(35A)	-23(3)
C(23B)	C(24)	C(25)	C(20)	-17.8(11)	N(9A)	C(33A)	C(34A)	C(40)	178.3(16)
C(26B)	C(23B)	C(24)	C(25)	-174.7(5)	N(10A)	C(36A)	C(37A)	C(38A)	-57(2)
C(27B)	C(28B)	C(29B)	N(8B)	179.8	C(45)	C(46)	C(47)	C(48)	1.8(12)
C(27B)	C(28B)	C(39B)	N(11B)	-175.5	C(45)	C(50)	O(1)	C(51)	169.6(6)
C(28B)	C(27B)	N(7B)	C(26B)	171.1	C(46)	C(45)	C(50)	C(49)	3.3(9)
C(28B)	C(29B)	N(8B)	C(30B)	-168.9	C(46)	C(45)	C(50)	O(1)	-173.2(6)

C(28B)	C(29B)	N(8B)	Ni(2B)	17.7	C(46)	C(45)	O(8)	C(68)	-0.9(9)
C(28B)	C(39B)	N(11B)	C(38B)	156.1	C(46)	C(47)	C(48)	C(49)	-1.4(13)
C(28B)	C(39B)	N(11B)	Ni(2B)	-21.1	C(47)	C(48)	C(49)	C(50)	2.0(12)
C(29B)	C(28B)	C(39B)	N(11B)	-17.1	C(48)	C(49)	C(50)	C(45)	-3.0(10)
C(30B)	C(31B)	C(32B)	N(9B)	65.1	C(48)	C(49)	C(50)	O(1)	173.3(7)
C(31B)	C(30B)	N(8B)	C(29B)	-122.5	C(49)	C(50)	O(1)	C(51)	-6.7(9)
C(31B)	C(30B)	N(8B)	Ni(2B)	51.2	C(50)	C(45)	C(46)	C(47)	-2.7(10)
C(31B)	C(32B)	N(9B)	C(33B)	113.1	C(50)	C(45)	O(8)	C(68)	179.6(6)
C(31B)	C(32B)	N(9B)	Ni(2B)	-63.4	C(51)	C(52)	O(2)	C(53)	-170.4(6)
C(32B)	N(9B)	Ni(2B)	N(8B)	41.8	C(52)	C(51)	O(1)	C(50)	-169.7(6)
C(32B)	N(9B)	Ni(2B)	N(10B)	-142.8	C(53)	C(54A)	O(3A)	C(55)	177.4(9)
C(33B)	C(34B)	C(35B)	N(10B)	23.8	C(53)	C(54B)	O(3B)	C(55)	-159.0(19)
C(33B)	C(34B)	C(40)	N(12)	-178.2(8)	C(54A)	C(53)	O(2)	C(52)	-168.2(9)
C(33B)	N(9B)	Ni(2B)	N(8B)	-134.4	C(54B)	C(53)	O(2)	C(52)	171.3(14)
C(33B)	N(9B)	Ni(2B)	N(10B)	41.1	C(55)	C(56)	O(4)	C(57)	-173.6(8)
C(34B)	C(33B)	N(9B)	C(32B)	167.1	C(56)	C(55)	O(3A)	C(54A)	-177.2(9)
C(34B)	C(33B)	N(9B)	Ni(2B)	-16.6	C(56)	C(55)	O(3B)	C(54B)	95(2)
C(34B)	C(35B)	N(10B)	C(36B)	-163.7	C(57)	C(58)	C(59)	C(60)	1.2(13)
C(34B)	C(35B)	N(10B)	Ni(2B)	16.3	C(57)	C(62)	O(5)	C(63)	169.6(6)
C(34B)	C(40)	N(12)	C(41B)	17.8(16)	C(58)	C(57)	C(62)	C(61)	2.6(10)
C(34B)	C(40)	N(12)	C(43)	-165.8(9)	C(58)	C(57)	C(62)	O(5)	-177.8(6)
C(35B)	C(34B)	C(40)	N(12)	13.0(13)	C(58)	C(57)	O(4)	C(56)	10.8(10)
C(35B)	N(10B)	Ni(2B)	N(9B)	-41.5	C(58)	C(59)	C(60)	C(61)	2.1(13)
C(35B)	N(10B)	Ni(2B)	N(11B)	134.8	C(59)	C(60)	C(61)	C(62)	-3.0(12)
C(36B)	C(37B)	C(38B)	N(11B)	62.9	C(60)	C(61)	C(62)	C(57)	0.5(10)
C(36B)	N(10B)	Ni(2B)	N(9B)	138.5	C(60)	C(61)	C(62)	O(5)	-179.0(6)
C(36B)	N(10B)	Ni(2B)	N(11B)	-45.2	C(61)	C(62)	O(5)	C(63)	-10.8(9)
C(37B)	C(36B)	N(10B)	C(35B)	-123.3	C(62)	C(57)	C(58)	C(59)	-3.5(12)
C(37B)	C(36B)	N(10B)	Ni(2B)	56.7	C(62)	C(57)	O(4)	C(56)	-170.8(6)
C(37B)	C(38B)	N(11B)	C(39B)	124.4	C(63)	C(64)	O(6)	C(65)	-176.1(6)
C(37B)	C(38B)	N(11B)	Ni(2B)	-58.6	C(64)	C(63)	O(5)	C(62)	-177.7(6)
C(38B)	N(11B)	Ni(2B)	N(8B)	-139.1	C(65)	C(66)	O(7)	C(67)	169.8(6)
C(38B)	N(11B)	Ni(2B)	N(10B)	45.6	C(66)	C(65)	O(6)	C(64)	172.1(6)
C(39B)	C(28B)	C(29B)	N(8B)	19.3	C(67)	C(68)	O(8)	C(45)	-170.2(7)
C(39B)	N(11B)	Ni(2B)	N(8B)	38.1	C(68)	C(67)	O(7)	C(66)	90.7(9)
C(39B)	N(11B)	Ni(2B)	N(10B)	-137.3	O(1)	C(51)	C(52)	O(2)	-73.7(8)
N(7B)	C(27B)	C(28B)	C(29B)	176.7	O(2)	C(53)	C(54A)	O(3A)	-47.9(12)
N(7B)	C(27B)	C(28B)	C(39B)	-20.6	O(2)	C(53)	C(54B)	O(3B)	55(3)
N(8B)	C(30B)	C(31B)	C(32B)	-58.4	O(3A)	C(55)	C(56)	O(4)	88.6(8)
N(9B)	C(33B)	C(34B)	C(35B)	-23.7	O(3B)	C(55)	C(56)	O(4)	52.5(16)
N(9B)	C(33B)	C(34B)	C(40)	166.7(5)	O(4)	C(57)	C(58)	C(59)	174.9(8)
N(10B)	C(36B)	C(37B)	C(38B)	-64.4	O(4)	C(57)	C(62)	C(61)	-176.0(6)
C(22A)	C(23A)	C(24)	C(25)	-13.7(14)	O(4)	C(57)	C(62)	O(5)	3.6(9)
C(22A)	C(23A)	C(26A)	N(7A)	-47.1(19)	O(5)	C(63)	C(64)	O(6)	-75.6(7)
C(23A)	C(24)	C(25)	C(20)	16.4(10)	O(6)	C(65)	C(66)	O(7)	68.8(8)
C(23A)	C(26A)	N(7A)	C(27A)	107.7(17)	O(7)	C(67)	C(68)	O(8)	71.6(10)
C(24)	C(23B)	C(26B)	N(7B)	168.2(8)	O(8)	C(45)	C(46)	C(47)	177.8(7)
C(24)	C(23A)	C(26A)	N(7A)	128.0(14)	O(8)	C(45)	C(50)	C(49)	-177.2(6)
C(25)	C(20)	C(21A)	C(22A)	3.4(10)	O(8)	C(45)	C(50)	O(1)	6.3(8)

C(25)	C(20)	C(21B)	C(22B)	-13.9(7)

Table 5S. The geometry of hydrogen bonds in the crystal of **6Ni$_2$**.

D–H	A	d(D···A) (Å)	< D–H···A (°)
N6–H6A	O2	2.842(7)	145
C12–H12	F19^{i}	3.405(9)	173
C13–H13	F24^{i}	3.055(12)	139
C14–H14A	F21^{ii}	3.199(13)	139
C14–H14B	F6B^{iii}	3.217(19)	132
C15–H15B	F24^{i}	3.316(18)	147
C16–H16A	F22	3.196(10)	142
C18–H18	O6	3.381(7)	144
C19–H19B	O7	3.217(8)	167
C25–H25	F18^{iv}	3.300(7)	158
C26A–H26C	F19^{iv}	2.936(16)	105
C32A–H32D	F16^{v}	3.32(2)	157
C40–H40	F11^{i}	3.335(10)	168
C41B–H41C	F8	2.95(2)	130
C41B–H41D	F12^{vi}	3.35(3)	155
C42B–H42F	F9	3.20(2)	133
C43–H43A	F12^{i}	3.401(14)	175
C52–H52B	F23	3.281(12)	137
C56–H56B	F7^{vi}	3.248(13)	141

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y, -z + 1$; (iii) $x, -y + 1/2, z - 1/2$; (iv) $x, -y + 1/2, z + 1/2$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $-x + 2, -y + 1, -z + 1$.

Table 6S. The geometry of the X−H···π interactions in the crystal of **6Ni$_2$**.

X−H	*Cg*I	d(X···*Cg*I) (Å)	<X−H···*Cg*I (°)
C30B−H30A	16^{vii}	3.685(8)	159

Symmetry code: (vii) $-x + 1, y + 1/2, -z + 3/2$.
*Cg*1 represents the centre of gravity of the C45–C50 aromatic ring (Figs 3 and 3S).