Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

On the nature of recurrent Au···π motifs in tris(2,2'-bipyridine)M(II) (M = Fe, Co and Ni) dicyanoaurate(I) salts: X-ray analysis and theoretical rationalization

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Figure S1 ORTEP plot of the asymmetric unit for compound **1.**

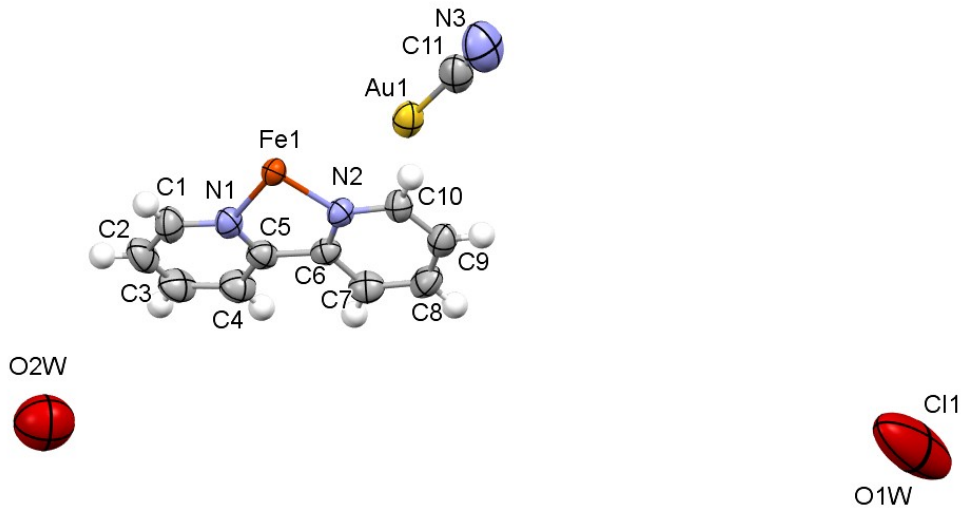

Table S1 Crystal data and structure refinement for compound **1.**

Identification code	**1**
Empirical formula	$C_{66}H_{48}Au_3ClFe_2N_{18}O_{11}$
Formula weight	2007.27
Temperature/K	293(2)
Crystal system	trigonal
Space group	R-3
a/Å	16.6981(5)
b/Å	16.6981(5)
c/Å	22.3503(8)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	5396.9(4)
Z	3
ρ_{calc}g/cm^3	1.853
μ/mm^{-1}	6.596
F(000)	2892.0
Crystal size/mm^3	0.560 × 0.320 × 0.250
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.712 to 64.36
Index ranges	$-16 \leq h \leq 23$, $-24 \leq k \leq 18$, $-31 \leq l \leq 26$
Reflections collected	8448
Independent reflections	3801 [R_{int} = 0.0495, R_{sigma} = 0.0677]

Data/restraints/parameters	3801/0/163
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0586, wR_2 = 0.1133
Final R indexes [all data]	R_1 = 0.1089, wR_2 = 0.1340
Largest diff. peak/hole / e Å^{-3}	2.14/-1.45

Table S2 Anisotropic Displacement Parameters (Å^2×10^3) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	83.5(3)	50.8(2)	47.8(2)	2.06(13)	-5.56(15)	31.60(19)
C11	103(6)	65(4)	61(4)	1(3)	-2(4)	47(4)
N3	139(7)	118(7)	77(4)	10(4)	28(5)	66(6)
Fe1	42.5(4)	42.5(4)	30.7(5)	0	0	21.3(2)
N1	60(3)	51(3)	35(2)	4.2(18)	5.9(19)	30(2)
N2	45(2)	48(3)	34.2(19)	3.2(17)	2.9(17)	22(2)
C1	77(5)	64(4)	47(3)	-6(3)	3(3)	37(4)
C2	96(6)	91(5)	49(3)	0(3)	16(3)	66(5)
C3	72(5)	103(6)	57(4)	12(3)	21(3)	58(5)
C4	59(4)	76(5)	64(4)	7(3)	10(3)	38(4)
C5	56(4)	58(4)	47(3)	6(2)	4(2)	34(3)
C6	43(3)	43(3)	47(3)	5(2)	-2(2)	21(2)
C7	48(3)	59(4)	66(4)	6(3)	4(3)	23(3)
C8	57(4)	50(4)	64(3)	-6(3)	-19(3)	19(3)
C9	68(4)	55(4)	45(3)	-2(3)	-5(3)	29(3)
C10	54(3)	46(3)	43(3)	-1(2)	3(2)	23(3)
Cl1	67(7)	80(8)	98(10)	12(7)	17(6)	32(7)
O1W	580(40)	510(40)	175(14)	97(18)	142(19)	470(30)
O2W	184(9)	186(9)	177(8)	22(6)	7(7)	96(8)

Table S3 Bond Lengths for **1.**

Table 4 Bond Lengths for FeAu1.						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Au1	C11[1]	1.978(9)		N2	C6	1.346(6)
Au1	C11	1.978(9)		N2	C10	1.351(6)
C11	N3	1.147(10)		C1	C2	1.383(9)
Fe1	N2	1.980(4)		C2	C3	1.366(10)
Fe1	N2[2]	1.980(4)		C3	C4	1.378(9)
Fe1	N2[3]	1.980(4)		C4	C5	1.395(8)
Fe1	N1[2]	1.986(4)		C5	C6	1.471(7)
Fe1	N1[3]	1.986(4)		C6	C7	1.377(8)
Fe1	N1	1.986(4)		C7	C8	1.393(8)
N1	C5	1.346(7)		C8	C9	1.382(9)
N1	C1	1.355(7)		C9	C10	1.381(8)

[1]1-X,2-Y,-Z; [2]1-Y,1+X-Y,+Z; [3]+Y-X,1-X,+Z

Table S4 Bond Angles for compound **1.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C11[1]	Au1	C11	180.0		C1	N1	Fe1	127.0(4)
N3	C11	Au1	178.5(8)		C6	N2	C10	116.6(5)
N2	Fe1	N2[2]	94.50(15)		C6	N2	Fe1	115.7(3)
N2	Fe1	N2[3]	94.50(15)		C10	N2	Fe1	127.6(4)
N2[2]	Fe1	N2[3]	94.50(15)		N1	C1	C2	122.5(6)
N2	Fe1	N1[2]	91.57(17)		C3	C2	C1	119.4(6)
N2[2]	Fe1	N1[2]	80.73(18)		C2	C3	C4	119.3(6)
N2[3]	Fe1	N1[2]	172.57(18)		C3	C4	C5	118.9(6)
N2	Fe1	N1[3]	172.57(18)		N1	C5	C4	122.3(5)
N2[2]	Fe1	N1[3]	91.57(17)		N1	C5	C6	114.1(4)
N2[3]	Fe1	N1[3]	80.73(18)		C4	C5	C6	123.6(6)
N1[2]	Fe1	N1[3]	93.64(17)		N2	C6	C7	122.9(5)
N2	Fe1	N1	80.73(18)		N2	C6	C5	113.8(5)
N2[2]	Fe1	N1	172.57(18)		C7	C6	C5	123.2(5)
N2[3]	Fe1	N1	91.57(17)		C6	C7	C8	119.8(6)
N1[2]	Fe1	N1	93.64(17)		C9	C8	C7	117.8(6)
N1[3]	Fe1	N1	93.64(17)		C10	C9	C8	119.1(5)
C5	N1	C1	117.5(5)		N2	C10	C9	123.6(5)
C5	N1	Fe1	115.2(3)					

[1]1-X,2-Y,-Z; [2]1-Y,1+X-Y,+Z; [3]+Y-X,1-X,+Z

Figure S2 ORTEP plot of the asymmetric unit for compound **2.**

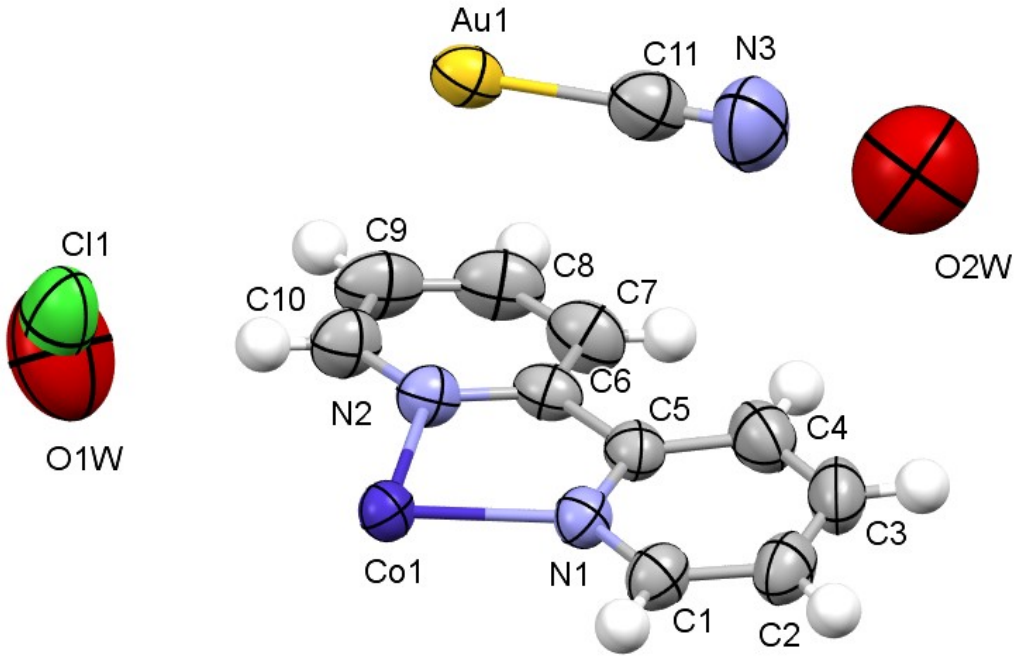

Table S5 Crystal data and structure refinement for compound **2.**

Identification code	**2**
Empirical formula	$C_{66}H_{48}Au_3ClCo_2N_{18}O_{11}$
Formula weight	2013.43
Temperature/K	293(2)
Crystal system	trigonal
Space group	R-3
a/Å	16.6621(11)
b/Å	16.6621(11)
c/Å	22.4615(10)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	5400.4(8)
Z	3
ρ_{calc}g/cm^3	1.857
μ/mm^{-1}	6.649
F(000)	2898.0
Crystal size/mm^3	0.45 × 0.30 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.318 to 64.672
Index ranges	-24 ≤ h ≤ 19, -24 ≤ k ≤ 24, -33 ≤ l ≤ 31
Reflections collected	11697
Independent reflections	3833 [R_{int} = 0.0447, R_{sigma} = 0.0415]
Data/restraints/parameters	3833/0/163
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0728
Final R indexes [all data]	R_1 = 0.0680, wR_2 = 0.0846
Largest diff. peak/hole / e Å^{-3}	1.80/-0.81

Table S6 Anisotropic Displacement Parameters (Å^2×10^3) for **2**. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Au1	48.48(14)	70.18(17)	46.85(13)	1.44(9)	-1.87(8)	27.31(11)
N3	109(4)	119(4)	87(3)	-32(3)	-8(3)	62(3)
C11	60(3)	88(3)	56(2)	-3(2)	-4.0(19)	33(2)
Co1	45.4(3)	45.4(3)	31.6(3)	0	0	22.70(14)
N1	48.2(16)	43.9(15)	36.8(13)	0.8(11)	1.5(12)	22.1(13)
N2	47.1(17)	54.1(18)	37.5(14)	-0.3(12)	-3.2(12)	23.6(14)
C1	58(2)	53(2)	41.2(18)	-2.6(15)	-3.8(16)	25.4(19)
C2	72(3)	55(2)	49(2)	-7.7(17)	3.8(19)	27(2)
C3	77(3)	58(2)	68(3)	-9(2)	12(2)	38(2)
C4	64(3)	67(3)	73(3)	2(2)	8(2)	40(2)
C5	46.7(19)	43.9(19)	45.9(18)	2.8(14)	5.0(14)	21.8(16)
C6	41.4(19)	53(2)	48.4(18)	9.5(15)	3.2(15)	22.4(17)
C7	63(3)	79(3)	68(3)	7(2)	-7(2)	43(2)
C8	59(2)	89(3)	61(2)	13(2)	-13(2)	35(2)

C9	58(2)	88(3)	47(2)	0(2)	-14.7(18)	23(2)
C10	61(2)	67(3)	47(2)	-5.0(18)	-8.8(17)	29(2)
Cl1	119(9)	109(9)	128(14)	-36(10)	-41(10)	79(8)
O2W	203(6)	185(6)	168(6)	8(4)	-13(4)	100(5)
O1W	231(12)	218(14)	100(5)	14(7)	23(6)	142(11)

Table S7 Bond Lengths for **2.**

Table 4 Bond Lengths for CoAu1c.						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Au1	C11[1]	1.986(5)		N2	C6	1.347(5)
Au1	C11	1.986(5)		C1	C2	1.382(6)
N3	C11	1.139(6)		C2	C3	1.372(6)
Co1	N2[2]	2.131(3)		C3	C4	1.373(6)
Co1	N2[3]	2.131(3)		C4	C5	1.396(5)
Co1	N2	2.131(3)		C5	C6	1.480(5)
Co1	N1	2.133(3)		C6	C7	1.390(5)
Co1	N1[3]	2.133(3)		C7	C8	1.374(6)
Co1	N1[2]	2.133(3)		C8	C9	1.355(6)
N1	C1	1.334(4)		C9	C10	1.394(6)
N1	C5	1.345(4)		Cl1	O1W	0.51(4)
N2	C10	1.334(4)				

[1]-X,1-Y,-Z; [2]+Y-X,1-X,+Z; [3]1-Y,1+X-Y,+Z

Table S8 Bond Angles for **2.**

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
C11[1]	Au1	C11	180.0(3)		C5	N1	Co1	115.3(2)
N3	C11	Au1	178.8(5)		C10	N2	C6	118.7(3)
N2[2]	Co1	N2[3]	95.23(10)		C10	N2	Co1	125.6(3)
N2[2]	Co1	N2	95.23(10)		C6	N2	Co1	115.1(2)
N2[3]	Co1	N2	95.22(10)		N1	C1	C2	123.8(4)
N2[2]	Co1	N1	93.02(11)		C3	C2	C1	118.0(4)
N2[3]	Co1	N1	169.30(11)		C2	C3	C4	119.4(4)
N2	Co1	N1	77.21(11)		C3	C4	C5	119.5(4)
N2[2]	Co1	N1[3]	169.30(11)		N1	C5	C4	121.3(3)
N2[3]	Co1	N1[3]	77.21(11)		N1	C5	C6	115.9(3)
N2	Co1	N1[3]	93.01(11)		C4	C5	C6	122.8(3)
N1	Co1	N1[3]	95.45(10)		N2	C6	C7	121.2(4)
N2[2]	Co1	N1[2]	77.21(11)		N2	C6	C5	115.7(3)
N2[3]	Co1	N1[2]	93.02(11)		C7	C6	C5	123.0(4)
N2	Co1	N1[2]	169.30(11)		C8	C7	C6	119.3(4)
N1	Co1	N1[2]	95.45(10)		C9	C8	C7	119.7(4)
N1[3]	Co1	N1[2]	95.45(10)		C8	C9	C10	118.8(4)
C1	N1	C5	117.9(3)		N2	C10	C9	122.3(4)
C1	N1	Co1	126.8(2)					

[1]-X,1-Y,-Z; [2]+Y-X,1-X,+Z; [3]1-Y,1+X-Y,+Z

Figure S3 ORTEP plot of the asymmetric unit for compound **3.**

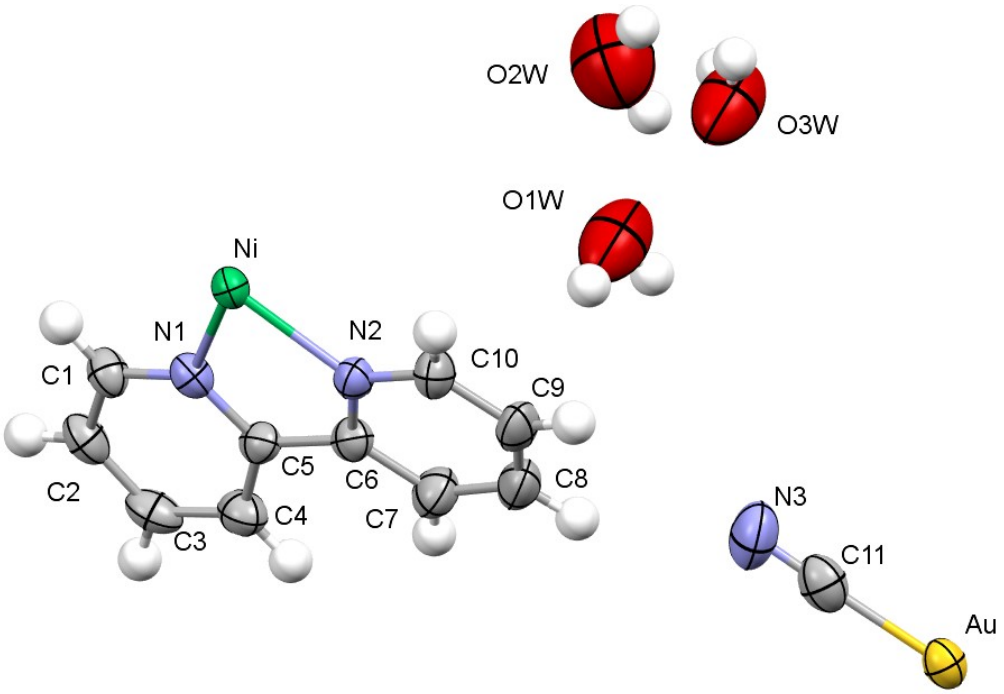

Table S9 Crystal data and structure refinement for compound **3.**

Identification code	**3**
Empirical formula	$C_{66}H_{73}Au_3N_{18}Ni_2O_{13}$
Formula weight	2035.75
Temperature/K	200(2)
Crystal system	trigonal
Space group	R-3
a/Å	16.4529(6)
b/Å	16.4529(6)
c/Å	22.4374(14)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	5260.0(5)
Z	3
ρ_{calc}g/cm^3	1.928
μ/mm^{-1}	6.857
F(000)	2979.0
Crystal size/mm^3	0.35 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.622 to 52.798
Index ranges	-19 ≤ h ≤ 20, -20 ≤ k ≤ 20, -27 ≤ l ≤ 27
Reflections collected	19600
Independent reflections	2405 [R_{int} = 0.0823, R_{sigma} = 0.0489]
Data/restraints/parameters	2405/0/156
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.0942

Final R indexes [all data]	R_1 = 0.0739, wR_2 = 0.1093
Largest diff. peak/hole / e Å^{-3}	1.92/-1.81

Table S10 Anisotropic Displacement Parameters (Å^2×10^3) for **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au	46.8(3)	51.1(3)	36.6(3)	0.86(18)	2.08(17)	30.2(2)
Ni	35.1(6)	35.1(6)	26.3(7)	0	0	17.6(3)
N1	40(3)	42(3)	32(3)	4(3)	4(3)	25(3)
N2	32(3)	42(4)	33(3)	-4(3)	-2(2)	17(3)
C1	53(5)	40(4)	32(4)	2(3)	1(3)	28(4)
C2	56(5)	57(5)	33(4)	10(3)	6(3)	36(4)
C3	55(5)	46(5)	52(5)	19(4)	18(4)	28(4)
C4	54(5)	40(4)	46(5)	4(4)	9(4)	19(4)
C5	37(4)	31(4)	38(4)	-4(3)	3(3)	15(3)
C6	39(4)	37(4)	38(4)	-4(3)	2(3)	19(3)
C7	53(5)	44(5)	51(5)	-9(4)	-8(4)	19(4)
C8	44(5)	61(6)	48(5)	-18(4)	-5(4)	18(4)
C9	35(4)	66(6)	43(5)	-12(4)	-11(3)	21(4)
C10	47(5)	50(5)	37(4)	-4(3)	-8(3)	22(4)
N3	74(6)	84(6)	63(5)	-29(5)	-18(4)	42(5)
C11	62(6)	68(6)	46(5)	0(4)	5(4)	43(5)
O1W	148(8)	75(5)	122(7)	6(5)	-50(6)	44(5)
O2W	192(12)	164(11)	138(9)	0(8)	-1(8)	97(10)
O3W	148(8)	75(5)	122(7)	6(5)	-50(6)	44(5)

Table S11 Bond Lengths for **3.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Au	C11[1]	1.984(10)		N2	C6	1.355(9)
Au	C11	1.984(10)		C1	C2	1.378(10)
Ni	N1[2]	2.091(6)		C2	C3	1.385(11)
Ni	N1	2.091(6)		C3	C4	1.378(11)
Ni	N1[3]	2.091(6)		C4	C5	1.391(10)
Ni	N2[2]	2.091(6)		C5	C6	1.465(10)
Ni	N2[3]	2.091(6)		C6	C7	1.393(10)
Ni	N2	2.091(6)		C7	C8	1.374(11)
N1	C1	1.336(9)		C8	C9	1.366(12)
N1	C5	1.351(9)		C9	C10	1.376(11)
N2	C10	1.331(9)		N3	C11	1.150(11)

[1]7/3-X,5/3-Y,5/3-Z; [2]1+Y-X,1-X,+Z; [3]1-Y,+X-Y,+Z

Table S12 Bond Angles for **3.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C11[1]	Au	C11	180.0		C10	N2	C6	118.9(6)
N1[2]	Ni	N1	94.5(2)		C10	N2	Ni	126.5(5)
N1[2]	Ni	N1[3]	94.5(2)		C6	N2	Ni	114.1(4)
N1	Ni	N1[3]	94.5(2)		N1	C1	C2	122.3(7)
N1[2]	Ni	N2[2]	78.9(2)		C1	C2	C3	119.1(7)
N1	Ni	N2[2]	170.1(2)		C4	C3	C2	119.2(7)
N1[3]	Ni	N2[2]	93.4(2)		C3	C4	C5	118.8(7)
N1[2]	Ni	N2[3]	170.1(2)		N1	C5	C4	121.7(7)
N1	Ni	N2[3]	93.3(2)		N1	C5	C6	116.1(6)
N1[3]	Ni	N2[3]	78.9(2)		C4	C5	C6	122.2(6)
N2[2]	Ni	N2[3]	94.0(2)		N2	C6	C7	120.8(7)
N1[2]	Ni	N2	93.3(2)		N2	C6	C5	116.0(6)
N1	Ni	N2	78.9(2)		C7	C6	C5	123.2(7)
N1[3]	Ni	N2	170.1(2)		C8	C7	C6	119.4(8)
N2[2]	Ni	N2	94.0(2)		C9	C8	C7	118.8(7)
N2[3]	Ni	N2	94.0(2)		C8	C9	C10	119.8(8)
C1	N1	C5	118.7(6)		N2	C10	C9	122.1(8)
C1	N1	Ni	126.9(5)		N3	C11	Au	178.2(9)
C5	N1	Ni	114.3(4)					

[1]7/3-X,5/3-Y,5/3-Z; [2]1+Y-X,1-X,+Z; [3]1-Y,+X-Y,+Z