Synthesis and reactions of N-heterocycle functionalised variants of heterometallic {Cr_7Ni} rings

George F. S. Whitehead,[1] Jesús Ferrando-Soria,[1] Laura Carthy,[1] Robin G. Pritchard,[1] Simon J. Teat,[2] Grigore A. Timco[1] and Richard E. P. Winpenny.[1]

1. *The School of Chemistry and Photon Science Institute, The University of Manchester, Oxford Road, Manchester M13 9PL*
2. *Advanced Light Source, Lawrence Berkeley Laboratory, 1 Cyclotron Road, MS2-400, Berkeley, California 94720, USA.*

Table of contents

1. Synthesis and experimental section

General experimental information contained within the main paper.

1.1 N-donor functionalised ring synthesis

1.1.1 Synthesis of [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_2H_2C_5H_4N)$] 2

[$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{16}$] (5.0 g, 2.18 mmol), 3-(4-pyridyl)acrylic acid (1.291 g, 8.77 mmol) and propan-1-ol (100 mL) were refluxed for 19.5 h with constant stirring. The resultant solution was cooled to room temperature and filtered. The solvent from the filtrate removed under reduced pressure and the resultant residue extracted in diethyl ether. The obtained solution was filtered and diethyl ether removed under reduced pressure leaving a green residue containing a mixture of unreacted and substituted products. **2** was separated and purified by column chromatography on 40-63 µm mesh silica gel (BDH). First, toluene was used as solvent, which allowed un-reacted starting ring to be eluted, leaving the products of the reaction at the top of the column. Thereafter a mixture of petroleum ether:ethyl acetate elution was used. Firstly, a 20:1 mixture was used to remove any remaining unreacted starting ring. This was then gradually worked up to an 8:1 mixture, eluting **2**. The solvent was removed under reduced pressure and the resultant residue recrystallized from ether/acetonitrile slow evaporation. Yield 0.628 g (12% based on [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{16}$]). Elemental anal. calculated (%) for $C_{89}H_{157}Cr_7F_8N_2NiO_{32}$: C45.65 H6.76 N1.20 Cr15.54; Found: C45.40 H6.88 N1.07 Cr15.49

1.1.2 Synthesis of [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_4H_3N_2)$] 3

[$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{16}$] (3.0 g, 1.31 mmol), 4-pyridazine acid (0.500 g, 4.10 mmol) and propan-1-ol (90 mL) were refluxed for 19.5 h with constant stirring. The resultant solution was cooled to room temperature and filtered. The solvent from the filtrate removed under reduced pressure and the resultant residue extracted in diethyl ether. The obtained solution was filtered and diethyl ether removed under reduced pressure leaving a green residue containing a mixture of unreacted and substituted products. **3** was separated and purified by column chromatography using a Reveleris® X2 Flash Chromatography System. First, toluene was used as solvent, which allowed un-reacted stating ring to be separated from the substituted products, leaving the products of the reaction at the top of the column. Thereafter a mixture of hexane:ethyl acetate elution was used. Firstly, a 20:1 mixture was used to elute unreacted starting ring, which was then ramped up to an 8:1 mixture, eluting **3**. Other bands, further substituted products, were also present on the column. The solvent was removed under reduced pressure and **3** was recrystallized from hot acetone. Yield 1.25 g (41.3% based on [$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{16}$]). Elemental anal. calculated (%) for $C_{86}H_{154}Cr_7F_8N_3NiO_{32}$: C44.58 H6.70 N1.81 Cr15.71; Found: C44.70 H7.05 N1.76 Cr15.52

1.2 Coordination compounds with rings as ligands

1.2.1 Synthesis of {[$^{n}Pr_2NH_2$][$Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)$]}$_2$[$Cu(NO_3)_2(OH_2)$] 4

$Cu(NO_3)_2.2.5H_2O$ (0.011g, 0.049 mmol) was added to a solution of **1** (0.3 g, 0.13 mmol) in hot acetone (30 mL) with stirring. The solution was refluxed for 5 minutes before cooling and left undisturbed in a sealed flask at room temperature. Dark green crystals suitable for single crystal XRD formed after 1 week and were collected by filtration and washed with acetone. Yield 0.17g (71.7% based on $Cu(NO_3)_2.2.5H_2O$). Elemental anal. calculated (%) for $C_{174}H_{312}Cr_{14}Cu_1F_{16}N_6Ni_2O_{71}$: C43.20 H6.50 N1.74 Cr15.05 Ni2.43 Cu1.31; Found: C43.05 H6.54 N1.66 Cr15.25 Ni2.42 Cu1.26

1.2.2 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[AgNO_3]$ 5

$AgNO_3$ (0.009 g, 0.053 mmol) was added to a solution of **1** (0.25 g, 1.08 mmol) in hot acetone (30 mL) with stirring. The solution was stirred for 24 h at ambient temperature, after which a precipitate formed. This was collected by filtration, redissolved in hot acetone and left to crystallise overnight. Small green crystals suitable for single crystal XRD formed. These were analysed and the remainder which were collected by filtration and washed with cold acetone. Yield 0.017g (6.68% based on $Ag(NO_3)$). Elemental anal. calculated (%) for $C_{174}H_{310}AgCr_{14}F_{16}N_5Ni_2O_{67}$: C43.59 H6.52 N1.46; Found: C43.65 H6.63 N1.40

1.2.3 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_2H_2C_5H_4N)]\}_2[Cu(NO_3)_2(OH_2)]$ 6

$Cu(NO3)_2{\cdot}2.5H_2O$ (0.012 g, 0.050 mmol) was added to a solution of **2** (0.302 g, 0.129 mmol) in hot acetone (40 mL) with constant stirring. The solution was refluxed for 5 mins after which it was cooled to room temperature and left in a sealed flask for 48h, after which crystals suitable for single crystal XRD formed. These were analysed and the remainder were collected and washed with cold acetone. Yield 0.126g (52% based on $Cu(NO3)_2{\cdot}2.5H_2O$). Elemental anal. calculated (%) for $C_{178}H_{316}Cr_{14}CuF_{16}N_6Ni_2O_{71}$: C43.73 H6.51 N1.72 Cr14.89 Ni2.40 Cu1.30; Found: C43.51 H6.55 N1.71 Cr14.94 Ni2.35 Cu1.23

1.2.4 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Ni(acac)_2]$ 7

$Ni(acac)_2{\cdot}2H_2O$ (0.063 g, 0.021 mmol) was added to a solution of **1** (0.100 g, 0.043 mmol) in hot acetone (20 mL) with constant stirring. The solution was refluxed for 5 mins, cooled and left covered. After 24 hours crystals formed. These were collected by filtration and washed with acetone. Yield 0.039 g (38% based on $Ni(acac)_2{\cdot}2H_2O$). Elemental anal. calculated (%) for $C_{184}H_{324}Cr_{14}F_{16}N_4Ni_3O_{68}$: C 45.21, H 6.68, N 1.15, Cr 14.89, Ni 3.60; Found: C 44.92, H 6.86, N 1.21, Cr 14.77, Ni 3.53

1.2.5 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Ni(F_3CCOCHCOCH_3)_2]$ 8

$Ni(F_3CCOCHCOCH_3)_2{\cdot}2H_2O$ (0.078g, 0.021 mmol) was added to a solution of **1** (0.100 g, 0.043 mmol) in hot acetone (20 mL) with constant stirring. The solution was refluxed for 5 mins, cooled and left covered. After 24 hours crystals formed. These were collected by filtration and washed with acetone. Yield 0.048 g (46% based on $Ni(F_3CCOCHCOCH_3)_2{\cdot}2H_2O$). Elemental anal. calculated (%) for $C_{184}H_{318}Cr_{14}F_{22}N_4Ni_3O_{68}$: C 44.23, H 6.42, N 1.12, Cr 14.57, Ni 3.52; Found: C 43.95, H 6.57, N 1.18, Cr 14.52, Ni 3.62

1.2.6 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Ni(Hfac)_2]$ 9

$Ni(Hfac)_2{\cdot}2H_2O$ (0.010 g, 0.021 mmol) was added to a solution of **1** (0.100 g, 0.043 mmol) in hot acetone (20 mL) with constant stirring. The solution was refluxed for 5 mins, cooled and left covered.

After 24 hours crystals formed. These were collected by filtration and washed with acetone. Yield 0.046 g (43% based on $Ni(Hfac)_2{\cdot}2H_2O$). Elemental anal. calculated (%) for $C_{184}H_{312}Cr_{14}F_{28}N_4Ni_3O_{68}$: C 43.30, H 6.16, N 1.09, Cr 14.26, Ni 3.45; Found: C 43.02, H 6.37, N 1.08, Cr 14.02, Ni 3.36

1.2.7 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Cu(Hfac)_2]$ 10

$Cu(Hfac)_2(H_2O)_2$ (0.011 g, 0.021 mmol) was added to a solution of **1** (0.101 g, 0.043 mmol) in hot acetone (20 mL) with constant stirring. The solution was refluxed for 5 mins, during which time a precipitate formed. This was collected by filtration, washed with acetone, dried in air and recrystallized from ether/acetone slow evaporation. Yield 0.046g (42.9% based on $Cu(Hfac)_2(H_2O)_2$). Elemental anal. calculated (%) for $C_{184}H_{312}Cr_{14}CuF_{28}N_4Ni_2O_{68}$: C43.25 H6.15 N1.10 Cr14.25 Ni2.30 Cu 1.24; Found: C43.15 H6.18 N1.11 Cr13.92 Ni2.29 Cu 1.23

1.2.8 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Mn(Hfac)_2]$ 11

$Mn(Hfac)_2(H_2O)_2$ (0.010 g, 0.021 mmol) was added to a solution of **1** (0.103 g, 0.044 mmol) in hot acetone (20 mL) with constant stirring. The solution was refluxed for 5 mins and then filtered hot. The solution was left partially covered and after partial evaporation crystals suitable for single crystal XRD formed. These were analysed and the remainder were collected and washed with acetone. Yield 0.052g (48.6% based on $Mn(Hfac)_2(H_2O)_2$). Elemental anal. calculated (%) for $C_{184}H_{312}Cr_{14}F_{28}MnN_4Ni_2O_{68}$: C43.33 H6.17 N1.10 Cr14.27 Ni2.30 Mn1.08; Found: C43.12 H6.23 N1.09 Cr14.08 Ni2.33 Mn1.02

1.2.9 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_4H_3N_2)]\}_2[Ni(Hfac)_2]$ 12

$Ni(Hfac)_2{\cdot}2H_2O$ (0.010 g, 0.021 mmol) was added to a solution of **3** (0.103 g, 0.044 mmol) in hot acetone (20 mL) with constant stirring. The solution was refluxed for 5 mins, cooled and left covered. After 24 hours crystals formed. These were collected by filtration and washed with acetone. Yield 0.042 g (39% based on $Ni(Hfac)_2{\cdot}2H_2O$). Elemental anal. calculated (%) for $C_{182}H_{310}Cr_{14}F_{28}N_6Ni_3O_{68}$: C 42.81, H 6.12, N 1.65, Cr 14.26, Ni 3.45; Found: C 42.47, H 6.00, N 1.59, Cr 13.85, Ni 3.46

1.2.10 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_4H_4N_2)]\}_2[Mn(Hfac)_2]$ 13

$Mn(Hfac)_2(H_2O)_2$ (0.014 g, 0.023 mmol) was dissolved in acetone (5 mL) and added to a solution of **3** (0.106g, 0.046 mmol) in hot acetone (15 mL) with constant stirring. The solution was refluxed for 5 mins, after which it was cooled to room temperature and sealed. Very small crystals formed after 48h, were collected by filtration and washed with acetone. Yield 0.056 g (47% based on $Mn(Hfac)_2{\cdot}2H_2O$). Elemental anal. calculated (%) for $C_{182}H_{310}Cr_{14}MnF_{28}N_6Ni_2O_{68}$: C43.27 H6.22 N1.61 Cr13.95 Mn1.05; Found: C43.15 H6.19 N1.66 Cr13.64 Mn0.80

1.2.11 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[ReCl(CO)_3]$ 14

$ReCl(CO)_5$ (0.031 mg, 0.085 mmol) was added to **1** (499 mg, 0.22 mmol) in toluene (10 ml) for 24 h. The solution was refluxed for 24h, after which the solution was cooled to room temperature and the toluene removed under reduced pressure. Column chromatography on alumina was used to isolate **31**, which was the first green band to be brought off using toluene as an eluent. The solvent was removed under reduced pressure and the residue recrystallised by acetone/pentane slow evaporation. Yield 0.263 g (62.7% based on $ReCl(CO)_5$). Elemental anal. calculated (%) for

$C_{177}H_{310}ClCr_{14}F_{16}N_4Ni_2O_{67}Re$: C43.06 H6.33 N1.13 Cr14.74 Re3.77; Found: C42.77 H6.32 N1.07 Cr14.46 Re3.85

1.2.12 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Cu_2(O_2C^tBu)_4]$ 15

$Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$ (0.038g, 0.052 mmol) was added to a solution of **1** (0.25 g, 0.11 mmol) in toluene (10 mL) with stirring. The solution was stirred at ambient temperature for 30 mins then refluxed for 10 mins. The solution was filtered hot, allowed to cool slowly and left at 35-40°C overnight. The flask was left sealed at room temperature for 2 days, after which time dark green crystals suitable for single crystal XRD formed. These were collected by filtration and washed with hexane. Yield 0.240 g (89.9% based on $Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$). Elemental anal. calculated (%) for $C_{194}H_{346}Cr_{14}Cu_2F_{16}N_4Ni_2O_{72}$: C45.13 H6.75 N1.09 Cr14.10 Ni2.27 Cu2.46; Found: C44.98 H6.87 N1.07 Cr14.39 Ni2.23 Cu2.43

1.2.13 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Ni_2(O_2C^tBu)_4]$ 16

$[Ni_2(\mu\text{-}H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$ (0.1 g, 0.105 mmol) was added to a solution of **1** (0.5 g, 0.22 mmol) in hot heptane (20 mL) with constant stirring. The solution was refluxed for 5 minutes, after which time a microcrystalline product formed. This was collected and washed with hot heptane and dried in air. Additional crystals suitable for single crystal XRD formed from the mother solution. Yield 0.210 g (38.5% based on $[Ni_2(\mu\text{-}H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$). Elemental anal. calculated (%) for $C_{196}H_{336}Cr_{14}F_{16}N_6Ni_4O_{72}$: C45.21 H6.77 N1.09 Cr14.13 Ni4.56; Found: C44.99 H6.67 N1.01 Cr13.71 Ni4.78

1.2.14 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Co_2(O_2C^tBu)_4]$ 17

$[Co_2(\mu\text{-}H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$ (0.027 g, 0.028 mmol) was dissolved in acetone (5 mL) and added to a solution of **1** (0.14 g, 0.06 mmol) in hot acetone (15 mL) with constant stirring. The solution was refluxed for 10 minutes, after which the solution was left to cool to room temperature and the flask sealed. Crystals suitable for single crystal XRD formed overnight, were analysed and the remainder were collected by filtration and washed with cold acetone. Yield 0.130 g (89.6% based on $[Co_2(\mu\text{-}H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$). Elemental anal. calculated (%) for $C_{196}H_{336}CoCr_{14}F_{16}N_6Ni_2O_{72}$: C45.21 H6.77 N1.08 Cr14.12 Ni2.28 Co2.29; Found: C45.15 H6.74 N1.11 Cr14.03 Ni2.17 Co2.42

1.2.15 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Ru_2(O_2C^tBu)_4]BF_4$ 18

$[Ru_2(O_2C^tBu)_4]BF_4$ (0.07 g, 0.101 mmol) was added to a solution of **1** (0.5 g, 0.22 mmol) in chloroform (5 mL), to which toluene (5 mL) was added. The solution was stirred for 5 mins and left open under a stream of nitrogen overnight. Hexane (10 mL) was added to the residue and stirred for 1h, after which the solution was filtered. The solid was collected, washed with hexane and recrystallized from chloroform/toluene slow evaporation. Yield 0.35 g (65.4% based on $[Ru_2(O_2C^tBu)_4]BF_4$). Elemental anal. calculated (%) for $C_{194}H_{346}B_1Cr_{14}F_{20}N_4Ni_2O_{72}Ru_2$: C43.76 H6.55 Cr13.67 Ni2.20; Found: C43.75 H6.60 Cr13.40 Ni2.12

1.2.16 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_5H_4N)]\}_2[Rh_2(O_2CCH_3)_4]$ 19

$Rh_2(O_2CCH_3)_4$ (0.03 g, 0.068 mmol) was dissolved in 10 mL of THF. To this, **1** (0.55 g, 0.24 mmol) and 5 mL of THF were added and the solution stirred for 30 mins. After this, the solution was filtered and

to the filtrate 5 mL of toluene was added. The solution was left stirring under a stream of nitrogen for two days, after which all the solvent had been removed. Hexane (15 mL) was added to the residue and stirred for 1h, after which the solution was filtered. The solid was collected, washed with hexane and recrystallized from THF/toluene slow evaporation. Yield 0.31 g (89.9% based on $Rh_2(O_2CCH_3)_4$). Elemental anal. calculated (%) for $C_{182}H_{322}Cr_{14}F_{16}N_4Ni_2O_{72}Rh_2$: C43.08 H6.40 N1.10 Cr14.35 Ni2.31 Rh4.06; Found: C43.43 H6.56 N1.09 Cr14.38 Ni2.25 Rh3.96

1.2.17 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_2H_2C_5H_4N)]\}_2[Cu_2(O_2C^tBu)_4]$ 20

$Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$ (0.038 g, 0.052 mmol) was added to a solution of **2** (0.253 g, 0.108 mmol) in toluene (10 mL) with constant stirring. The solution was stirred at ambient temperature for 15 mins and refluxed for 5 mins. After this it was cooled to room temperature and left to slowly evaporate, after which crystals suitable for single crystal XRD formed. These were analysed and the remainder were collected and washed with acetone. Yield 0.038 g (17% based on $Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$). Elemental anal. calculated (%) for $C_{198}H_{350}Cr_{14}Cu_2F_{16}N_4Ni_2O_{72}$: C45.60 H6.76 N1.07 Cr13.96 Cu2.44; Found: C45.70 H6.85 N1.02 Cr13.59 Cu2.48

1.2.18 Synthesis of $\{[^nPr_2NH_2][Cr_7NiF_8(O_2C^tBu)_{15}(O_2CC_4H_3N_2)]\}_2[Cu_2(O_2C^tBu)_4]$ 21

$Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$ (0.039 g, 0.053 mmol) was added to a solution of **3** (0.250g, 0.108 mmol) in toluene (10 mL) with constant stirring. The solution was stirred at ambient temperature for 15 mins and refluxed for 5 mins. After this it was cooled to room temperature and left to slowly evaporate, after which crystals single crystal XRD formed. These were analysed and the remainder were collected by filtration and washed with acetone. Yield 0.125 g (44% based on $Cu_2(O_2C^tBu)_4(HO_2C^tBu)_2$). Elemental anal. calculated (%) for $C_{192}H_{344}Cr_{14}Cu_2F_{16}N_6Ni_2O_{72}$: C44.65 H6.71 N1.63 Cr14.09 Cu2.46; Found: C44.78 H6.84 N1.51 Cr13.27 Cu2.47

2. Crystallographic information

Table S1. Structural metrics for all compounds

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{87}H_{155}Cr_7F_8N_2NiO_{32}$	$C_{89}H_{157}Cr_7F_8N_2NiO_{32}$	$C_{86}H_{154}Cr_7F_8N_3NiO_{32}$	$C_{351}H_{626}Cr_{28}Cu_2F_{32}N_{12}Ni_4O_{142.50}$	$C_{177}H_{316}AgCr_{14}F_{16}N_5Ni_2O_{68}$
M_r	2315.84	2341.88	2316.82	9720.56	4859.54
Crystal System	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space Group	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1	$Pna2_1$
a [Å]	25.141 (3)	25.2879 (14)	25.4134 (6)	16.5633 (6)	33.3454 (10)
b [Å]	17.059 (2)	16.7259 (9)	16.6467 (4)	34.1024 (10)	16.4902 (5)
c [Å]	30.727 (4)	30.8206 (15)	31.7318 (7)	48.3068 (19)	49.2045 (16)
α [°]	90	90	90	83.3020 (10)	90
β [°]	106.127 (2)	109.154 (6)	108.992 (2)	87.7560 (10)	90
γ [°]	90	90	90	90.499 (3)	90
V [Å^3]	12659 (3)	12314.3 (11)	12693.4 (5)	27078.3 (17)	27056.2 (15)
Z	4	4	4	2	4
ρ_{calcd} [mg mm^{-3}]	1.215	1.263	1.212	1.192	1.193
T [K]	150	100	150	150	100
Goof on F^2	1.029	1.02	1.09	1.423	1.087
R_1 [$I>2\sigma(I)$]	0.0986	0.0812	0.1296	0.1399	0.1071
wR_2 [all data]	0.1416	0.2323	0.3419	0.3331	0.2904

Compound	**6**	**7**	**8**	**9**	**10**
Formula	$C_{196}H_{352}Cr_{14}CuF_{16}N_6Ni_2O_{78}$	$C_{186}H_{324}Cr_{14}F_{16}N_5Ni_3O_{68}$	$C_{184}H_{318}Cr_{14}F_{22}N_4Ni_3O_{68}$	$C_{184}H_{312}Cr_{14}F_{28}N_4Ni_3O_{68}$	$C_{184}H_{312}Cr_{14}CuF_{28}N_4Ni_2O_{68}$
M_r	5253.75	4921.51	4996.51	5104.46	5109.32
Crystal System	triclinic	monoclinic	monoclincic	monoclinic	triclinic
Space Group	P-1	$P2_1/c$	C2/c	C2/c	P-1
a [Å]	16.4760 (3)	48.647(2)	60.078(3)	60.628(4)	16.4384 (6)
b [Å]	25.5232 (5)	16.5985(5)	16.6492(7)	16.8601(4)	16.7162 (6)
c [Å]	33.6920 (5)	34.1665(11)	30.617(2)	30.7889(13)	26.8666 (12)
α [°]	96.7720 (10)	90	90	90	99.150 (3)
β [°]	90.4410 (10)	96.152(3)	111.154(7)	111.487	98.927 (3)
γ [°]	105.705 (2)	90	90	90	112.035 (2)
V [Å^3]	13532.4 (4)	27429.7(17)	28561(3)	29285(2)	6567.5 (4)
Z	2	4	4	4	1
ρ_{calcd} [mg mm^{-3}]	1.289	1.193	1.162	1.158	1.292
T [K]	100	100	100	100	90
Goof on F^2	1.12	1.002	0.996	1.087	1.059
R_1 [$I>2\sigma(I)$]	0.0914	0.0742	0.0913	0.1208	0.0685
wR_2 [all data]	0.252	0.2428	0.2781	0.3823	0.2098

Table S1. contd.

Compound	**11**	**12**	**14**	**15**	**16**
Formula	$C_{184}H_{312}Cr_{14}F_{28}MnN_4Ni_2O_{68}$	$C_{182}H_{312}Cr_{14}F_{28}N_6Ni_3O_{68}$	$C_{177}H_{310}ClCr_{14}F_{16}N_4Ni_2O_{67}Re$	$C_{208}H_{362}Cr_{14}Cu_2F_{16}N_4Ni_2O_{74}$	$C_{200}H_{358}Cr_{14}F_{16}N_4Ni_4O_{74}$
M_r	5100.71	2106.51	4937.27	5379.52	5269.68
Crystal System	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space Group	P-1	Pccn	$P2_1/c$	C2/c	Pnnm
a [Å]	16.5428 (5)	55.0070 (14)	30.477 (5)	60.9040 (8)	47.9643 (14)
b [Å]	16.6931 (5)	17.2341 (4)	16.591 (3)	16.9000 (2)	16.6262 (5)
c [Å]	26.9382 (11)	30.5232 (8)	53.880 (8)	30.7200 (5)	26.0764 (8)
α [°]	99.731 (2)	90	90	90	90
β [°]	98.643 (2)	90	99.480 (2)	103.8030 (10)	90
γ [°]	111.648 (2)	90	90	90	90
V [Å^3]	6628.7 (4)	28935.9 (13)	26872 (7)	30706.3 (7)	20795.0 (11)
Z	1	2	4	4	2
ρ_{calcd} [mg mm^{-3}]	1.278	1.172	1.22	1.164	0.842
T [K]	90	100	150	150	100
Goof on F^2	1.09	1.122	0.997	1.264	1.124
R_1 [$I>2\sigma(I)$]	0.08	0.0588	0.1562	0.0981	0.1564
wR_2 [all data]	0.24	0.1876	0.4007	0.2669	0.4114

Compound	**17**	**18**	**19**	**20**	**21**
Formula	$C_{194}H_{346}Co_2Cr_{14}F_{16}N_4Ni_2O_{72}$	$B_1C_{196}H_{348}Cl_6Cr_{14}F_{20}N_4Ni_2O_{72}Ru_2$	$C_{182}H_{322}Cr_{14}F_{16}N_4Ni_2O_{72}Rh_2$	$C_{212}H_{366}Cr_{14}Cu_2F_{16}N_4Ni_2O_{72}$	$C_{192}H_{344}Cr_{14}Cu_2F_{16}N_6Ni_2O_{72}$
M_r	5154.01	5563.8	5073.68	5399.59	5165.23
Crystal System	tetragonal	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$I4_1/a$	C2/c	C2/c	$P2_1/c$	C2/c
a [Å]	58.317 (6)	61.511 (3)	56.127 (7)	31.2667 (15)	60.7106 (12)
b [Å]	58.317 (6)	17.0854 (5)	16.2525 (19)	17.5635 (9)	16.7468 (4)
c [Å]	16.7336 (18)	30.5948 (8)	31.418 (4)	30.8297 (15)	30.4987 (9)
α [°]	90	90	90	90	90
β [°]	90	104.182 (4)	111.474 (2)	117.007 (2)	103.9900 (9)
γ [°]	90	90	90	90	90
V [Å^3]	56908 (14)	31193.5 (19)	26670 (5)	15084.0 (13)	30088.5 (13)
Z	8	4	4	2	4
ρ_{calcd} [mg mm^{-3}]	1.203	1.166	1.264	1.189	1.14
T [K]	150	100	100	100	100
Goof on F^2	1.04	1.078	1.041	1.015	1.253
R_1 [$I>2\sigma(I)$]	0.0791	0.0816	0.0697	0.0805	0.1339
wR_2 [all data]	0.1616	0.2659	0.2173	0.264	0.4096