Supporting Information

Folded $Cr_{12}Co_{12}$ and $Cr_{12}Ni_{12}$ Wheels: A Sharp Increase in Nuclearity of Heterometallic Chromium Rings

Christian Plenk,[ab] Thomas Weyhermüller[c] and Eva Rentschler*[a]

a Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany. Fax: (+49) 6131-39-23922; E-mail: rentschl@uni-mainz.de

b Graduate School Materials Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany.

c Max-Planck-Institut für Chemische Energiekonversion, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany.

1. Experimental Section

The ligand 2,2'-bipyrimidine (bpym)[1] and the complexes $[Cr_3O(O_2CCMe_3)_6(H_2O)_3]O_2CCMe_3$,[2] $[Co_2(OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$[3] and $[Ni_2(OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$[4] were prepared following previously reported procedures. All other chemicals were reagent grade and used as received without further purification.

1: A suspension of $[Cr_3O(O_2CCMe_3)_6(H_2O)_3]O_2CCMe_3$ (0.367 g, 0.40 mmol), $[Co_2(OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$ (0.199 g, 0.21 mmol) and 2,2'-bipyrimidine (0.032 g, 0.20 mmol) in 20 ml of acetone was heated under reflux for 3 min. The resulting blue solution was filtered to remove insoluble solid material. The filtrate was left for slowly evaporating at room temperature and after 5 days X-ray-quality red crystals were formed which have been identified crystallographically as $[Cr_{12}Co_{12}(OH)_{16}(O_2CCMe_3)_{44}(HO_2CCMe_3)_4(bpym)_4]\cdot 13\ OC(CH_3)_2$ (**1**$\cdot 13\ OC(CH_3)_2$). The crystals were collected by filtration, washed with acetone and dried in vacuum. Yield: 0.085 g (24%). Selected IR data (KBr): $\tilde{\upsilon}$=2961 (m), 2928 (m), 2928 (m), 2870 (w), 1574 (s), 1557 (s), 1486 (s), 1427 (s), 1361 (m), 1230 (m), 786 (w), 610 cm^{-1} (m); Elemental analysis (AAS for Cr and Co) calcd. for $C_{272}H_{484}Co_{12}Cr_{12}N_{16}O_{116}$ (**1**$\cdot 4\ H_2O$): Cr 9.66, Co 9.87, C 45.59, H 6.81, N 3.13; found: Cr 8.62, Co 9.74, C 45.57, H 6.55, N 3.16.

2: A suspension of $[Cr_3O(O_2CCMe_3)_6(H_2O)_3]O_2CCMe_3$ (0.373 g, 0.41 mmol), $[Ni_2(OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$ (0.191 g, 0.20 mmol) and 2,2'-bipyrimidine (0.034 g, 0.22 mmol) in 20 ml of acetone was heated under reflux for 3 min. The resulting green solution was filtered to remove insoluble solid material. The filtrate was left for slowly evaporating at room temperature and after 18 days X-ray-quality green crystals were formed which have been identified crystallographically as

$[Cr_{12}Ni_{12}(OH)_{16}(O_2CCMe_3)_{44}(HO_2CCMe_3)_4(bpym)_4]\cdot 9\ OC(CH_3)_2$ (**2**$\cdot$9 $OC(CH_3)_2$). The crystals were collected by filtration, washed with acetone and dried in vacuum. Yield: 0.013 g (3%). Selected IR data (KBr): $\tilde{\upsilon}$=2961 (m), 2928 (m), 2928 (m), 2869 (w), 1604 (s), 1577 (s), 1558 (s), 1486 (s), 1429 (s), 1361 (m), 1232 (m), 787 (w), 611 cm^{-1} (m); Elemental analysis (AAS for Cr and Ni) calcd. for $C_{272}H_{480}Cr_{12}N_{16}Ni_{12}O_{114}$ (**2**$\cdot$2 H_2O): Cr 8.75, Ni 9.88, C 45.84, H 6.79, N 3.14; found: Cr 8.04, Ni 9.98, C 45.84, H 7.09, N 3.30.

2. X-Ray Structure Determination

Single crystals of **1** and **2** were coated with perfluoropolyether, picked up with nylon loops and mounted in the nitrogen cold stream of the diffractometer. Mo-Kα radiation (λ=0.71073Å) from a Mo-target rotating-anode X-ray source was used. Final cell constants were obtained from least squares fits of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections with the programs SADABS[5] for **1** and PLATON[6] for **2**. The structures were readily solved by Patterson methods and subsequent difference Fourier techniques. The Siemens ShelXTL[7] software package was used for solution of the structures, ShelXL2012[8] was used for the refinement. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters with the exception of hydrogen atoms of the hydroxo ligands in complex **1** which were located in the difference map. In both structures some pivalate groups appeared disordered and were modeled as two split positions with a refined occupation factor ratio.

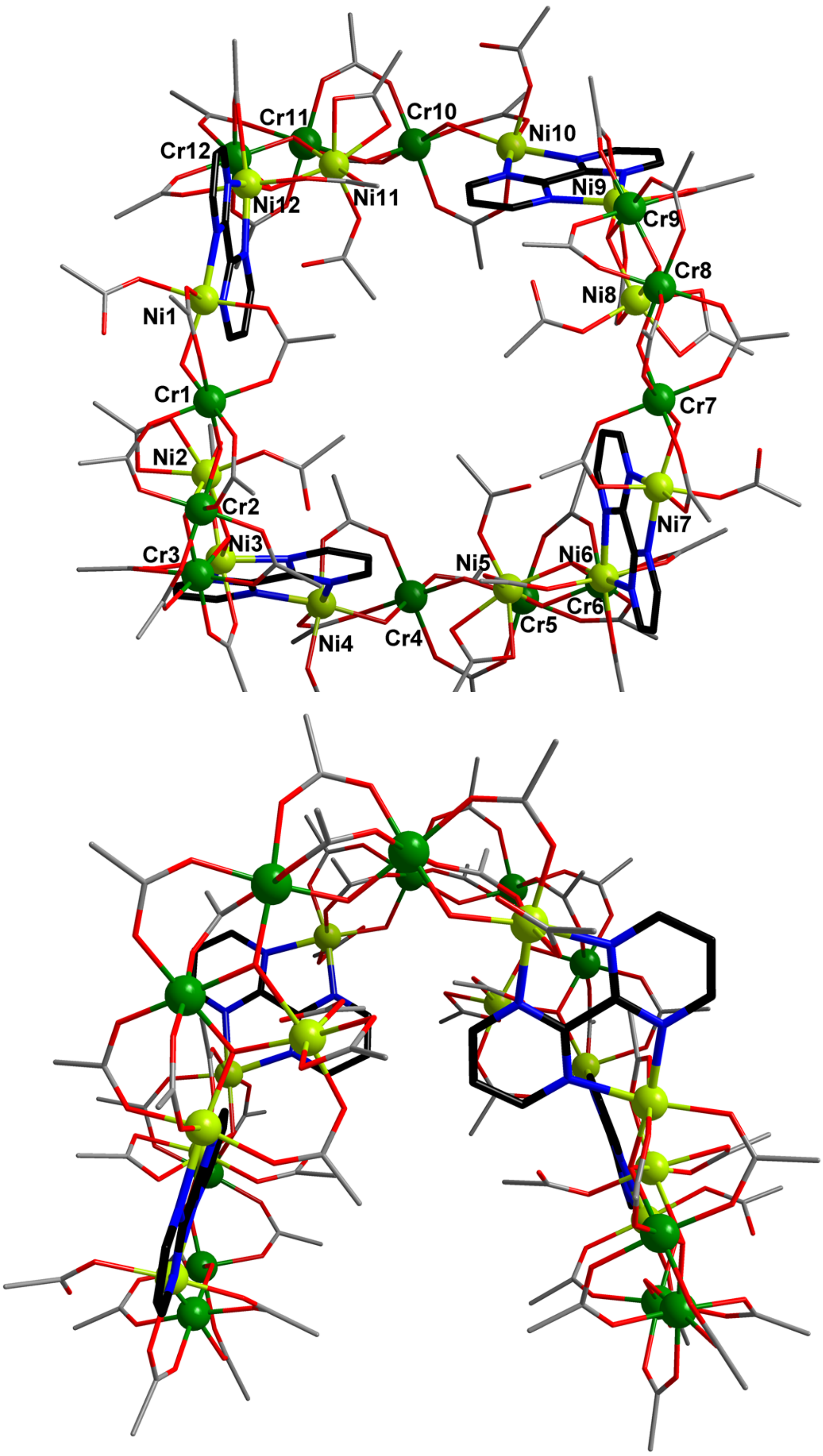

Figure S1. Top and side view of the molecular structure of $[Cr_{12}Ni_{12}(OH)_{16}(O_2CCMe_3)_{44}(HO_2CCMe_3)_4(bpym)_4]$ (**2**). Methyl groups of pivalates and hydrogen atoms are omitted for clarity and only selected atoms were labeled. Grey/Black (C), Red (O), Blue (N).

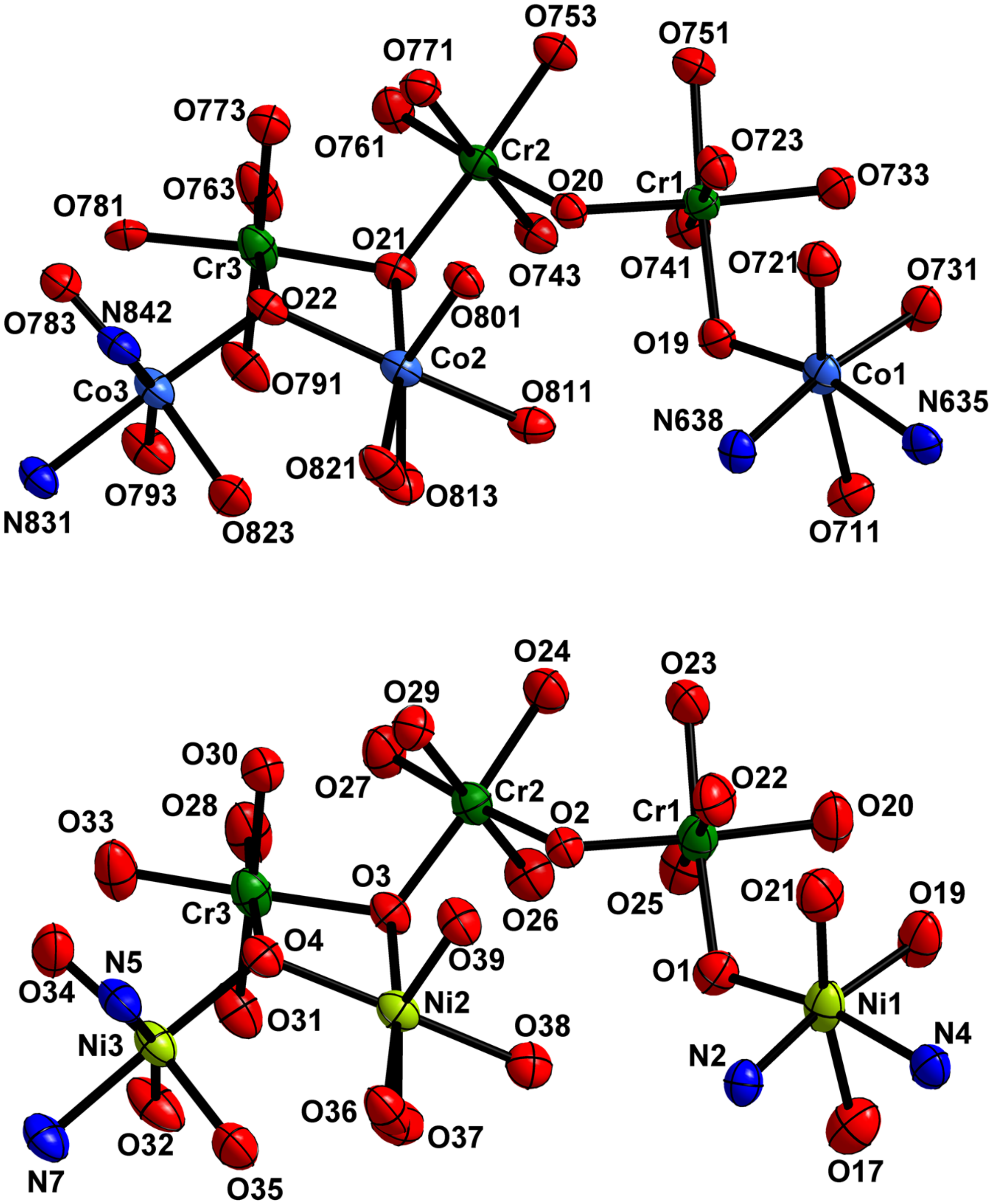

Figure S2. ORTEP representation (ellipsoids at 50% probability) of a selected Cr_3M_3 unit of complexes **1** (top) and **2** (bottom).

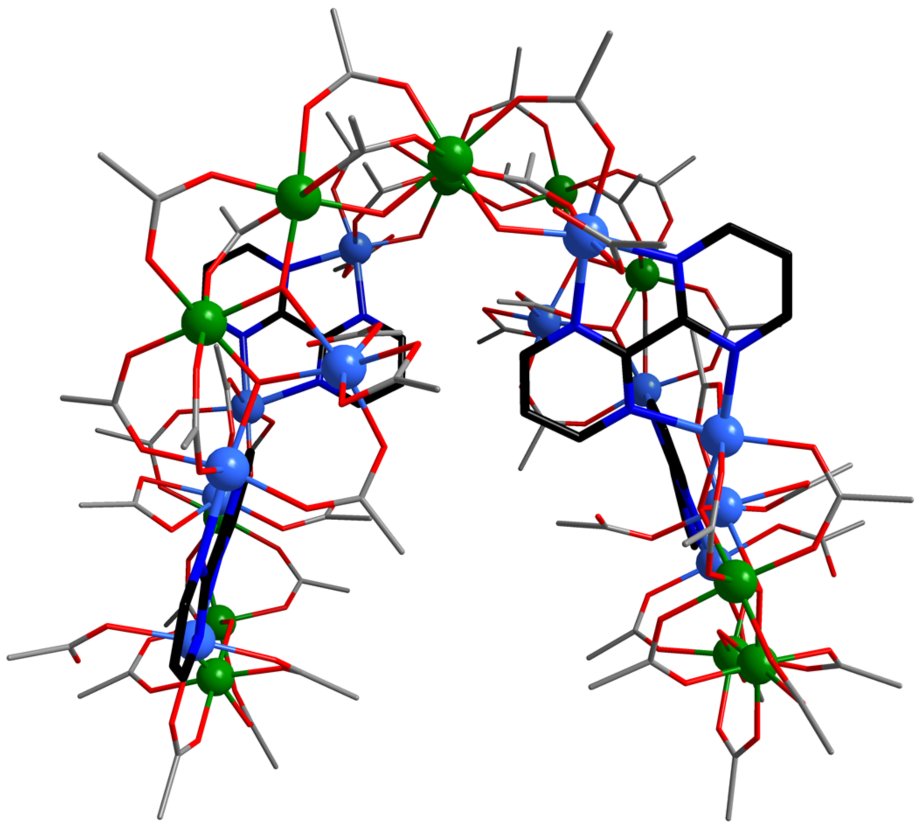

Figure S3. Side view of the molecular structure of $[Cr_{12}Co_{12}(OH)_{16}(O_2CCMe_3)_{44}(HO_2CCMe_3)_4(bpym)_4]$ (**1**). Methyl groups of pivalates and hydrogen atoms are omitted for clarity and only selected atoms were labeled. Light-blue (Co), Green (Cr), Grey/Black (C), Red (O), Blue (N).

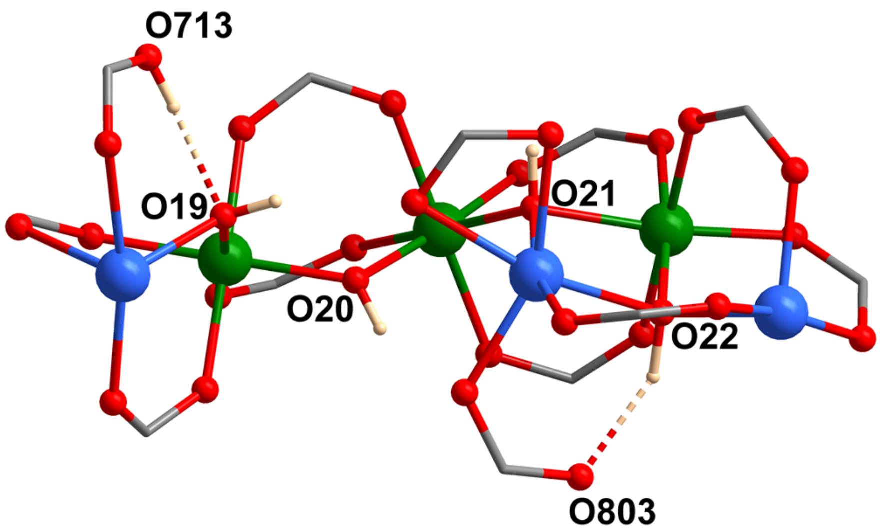

Figure S4. Representation of the bridging OH ligands and hydrogen bonds (dashed lines) in a selected Cr_3Co_3 core of complex **1**. Grey (C), Red (O), Light-blue (Co), Green (Cr).

Table S1: Selected bond lengths (Å) of **1**.

Cr1—O20	1.913 (5)	Co1—O721	2.020 (7)
Cr1—O723	1.962 (6)	Co1—O19	2.046 (6)
Cr1—O19	1.964 (6)	Co1—O731	2.050 (6)
Cr1—O733	1.973 (6)	Co1—N638	2.118 (7)
Cr1—O741	1.976 (6)	Co1—N635	2.128 (7)
Cr1—O751	1.983 (6)	Co1—O711	2.166 (6)
Cr2—O20	1.916 (6)	Co2—O821	2.045 (6)
Cr2—O753	1.972 (6)	Co2—O801	2.046 (5)
Cr2—O771	1.973 (6)	Co2—O22	2.109 (6)
Cr2—O743	1.977 (6)	Co2—O811	2.133 (6)
Cr2—O761	1.980 (6)	Co2—O813	2.180 (6)
Cr2—O21	1.985 (5)	Co2—O21	2.241 (5)
Cr3—O781	1.894 (16)	Co3—O823	2.010 (7)
Cr3—O791	1.941 (7)	Co3—O22	2.051 (5)
Cr3—O773	1.951 (6)	Co3—O783	2.061 (13)
Cr3—O22	1.958 (5)	Co3—O793	2.064 (6)
Cr3—O763	1.979 (6)	Co3—N831	2.150 (7)
Cr3—O21	2.000 (6)	Co3—N842	2.197 (7)
Cr4—O2	1.926 (5)	Co4—O121	2.013 (6)
Cr4—O1	1.964 (6)	Co4—O131	2.041 (6)
Cr4—O151	1.976 (6)	Co4—O1	2.042 (6)
Cr4—O123	1.978 (6)	Co4—N838	2.117 (7)
Cr4—O133	1.992 (6)	Co4—O111	2.127 (7)
Cr4—O141	1.992 (6)	Co4—N835	2.141 (7)
Cr5—O2	1.924 (5)	Co5—O201	2.022 (6)
Cr5—O171	1.959 (6)	Co5—O221	2.074 (5)
Cr5—O143	1.966 (6)	Co5—O4	2.108 (6)
Cr5—O3	1.970 (5)	Co5—O213	2.110 (6)
Cr5—O153	1.971 (6)	Co5—O211	2.171 (6)

Cr5—O161	1.992 (6)	Co5—O3	2.274 (5)
Cr6—O191	1.949 (6)	Co6—O223	2.021 (6)
Cr6—O4	1.950 (5)	Co6—O183	2.050 (6)
Cr6—O181	1.962 (7)	Co6—O4	2.053 (5)
Cr6—O173	1.969 (6)	Co6—O193	2.056 (6)
Cr6—O163	1.975 (6)	Co6—N231	2.189 (7)
Cr6—O3	2.003 (6)	Co6—N242	2.217 (7)
Cr7—O8	1.935 (5)	Co7—O321	2.033 (6)
Cr7—O7	1.949 (5)	Co7—O331	2.038 (6)
Cr7—O323	1.961 (6)	Co7—O7	2.069 (6)
Cr7—O333	1.975 (6)	Co7—N238	2.104 (7)
Cr7—O341	1.986 (6)	Co7—O311	2.142 (6)
Cr7—O351	1.991 (6)	Co7—N235	2.146 (7)
Cr8—O8	1.915 (5)	Co8—O401	2.053 (6)
Cr8—O371	1.953 (6)	Co8—O421	2.080 (6)
Cr8—O343	1.958 (5)	Co8—O10	2.090 (5)
Cr8—O9	1.965 (5)	Co8—O413	2.128 (6)
Cr8—O353	1.968 (5)	Co8—O411	2.160 (6)
Cr8—O361	1.996 (6)	Co8—O9	2.307 (5)
Cr9—O391	1.938 (6)	Co9—O423	2.035 (6)
Cr9—O10	1.954 (5)	Co9—O10	2.040 (5)
Cr9—O381	1.967 (6)	Co9—O383	2.052 (6)
Cr9—O373	1.967 (6)	Co9—O393	2.057 (6)
Cr9—O363	1.979 (6)	Co9—N431	2.169 (6)
Cr9—O9	1.999 (5)	Co9—N442	2.194 (6)
Cr10—O14	1.928 (5)	Co10—O521	2.024 (6)
Cr10—O523	1.953 (6)	Co10—O531	2.027 (6)
Cr10—O13	1.959 (5)	Co10—O13	2.054 (5)
Cr10—O533	1.978 (5)	Co10—N438	2.099 (6)
Cr10—O551	1.990 (6)	Co10—N435	2.124 (7)
Cr10—O541	1.993 (6)	Co10—O511	2.148 (6)

Cr11—O14	1.916 (5)	Co11—O601	2.052 (5)
Cr11—O561	1.944 (14)	Co11—O621	2.071 (6)
Cr11—O571	1.960 (6)	Co11—O611	2.102 (6)
Cr11—O543	1.961 (6)	Co11—O16	2.107 (5)
Cr11—O553	1.979 (5)	Co11—O613	2.165 (6)
Cr11—O15	1.981 (5)	Co11—O15	2.305 (5)
Cr12—O591	1.943 (7)	Co12—O623	2.010 (6)
Cr12—O16	1.963 (5)	Co12—O16	2.054 (5)
Cr12—O573	1.985 (6)	Co12—O593	2.058 (6)
Cr12—O15	1.994 (6)	Co12—O583	2.078 (15)
Cr12—O563	2.030 (16)	Co12—N631	2.185 (7)
Cr12—O581	2.040 (12)	Co12—N642	2.188 (7)

Table S2: Selected bond lengths (Å) of **2**.

O1—Cr1	1.961 (5)	O21—Ni1	2.018 (7)
O2—Cr1	1.928 (5)	O17—Ni1	2.121 (6)
O20—Cr1	1.974 (6)	O19—Ni1	2.028 (6)
O22—Cr1	1.956 (6)	O1—Ni1	2.045 (5)
O23—Cr1	1.972 (6)	O36—Ni2	2.033 (5)
O25—Cr1	1.989 (6)	O37—Ni2	2.136 (6)
O24—Cr2	1.974 (5)	O38—Ni2	2.118 (5)
O26—Cr2	1.983 (6)	O39—Ni2	2.027 (5)
O27—Cr2	1.985 (5)	O4—Ni2	2.091 (5)
O29—Cr2	1.967 (5)	O3—Ni2	2.224 (5)
O3—Cr2	1.988 (5)	O34—Ni3	2.037 (6)
O2—Cr2	1.916 (5)	O35—Ni3	1.991 (6)
O28—Cr3	1.979 (6)	O32—Ni3	2.017 (6)
O30—Cr3	1.969 (6)	O4—Ni3	2.017 (5)
O31—Cr3	1.947 (6)	O5—Ni4	2.041 (5)

O33—Cr3	1.966 (6)	O45—Ni4	2.010 (6)
O3—Cr3	2.006 (5)	O41—Ni4	2.116 (6)
O4—Cr3	1.969 (5)	O43—Ni4	2.005 (5)
O5—Cr4	1.973 (5)	O60—Ni5	2.038 (5)
O6—Cr4	1.934 (5)	O61—Ni5	2.107 (6)
O44—Cr4	1.984 (5)	O62—Ni5	2.134 (5)
O46—Cr4	1.968 (6)	O63—Ni5	2.010 (5)
O47—Cr4	2.014 (6)	O8—Ni5	2.074 (5)
O49—Cr4	1.991 (6)	O7—Ni5	2.226 (5)
O48—Cr5	1.983 (5)	O56—Ni6	2.026 (5)
O50—Cr5	1.977 (5)	O58—Ni6	2.044 (6)
O51—Cr5	2.002 (6)	O59—Ni6	2.008 (6)
O53—Cr5	1.964 (6)	O8—Ni6	2.036 (5)
O6—Cr5	1.931 (5)	O9—Ni7	2.047 (5)
O7—Cr5	1.984 (5)	O69—Ni7	2.037 (6)
O52—Cr6	1.980 (6)	O65—Ni7	2.128 (6)
O54—Cr6	1.960 (6)	O67—Ni7	2.016 (5)
O55—Cr6	1.951 (6)	O84—Ni8	2.049 (5)
O57—Cr6	1.948 (6)	O85—Ni8	2.101 (6)
O7—Cr6	2.006 (5)	O86—Ni8	2.125 (5)
O8—Cr6	1.949 (5)	O87—Ni8	2.029 (5)
O9—Cr7	1.963 (5)	O12—Ni8	2.060 (5)
O68—Cr7	1.977 (5)	O11—Ni8	2.257 (5)
O70—Cr7	1.964 (5)	O82—Ni9	2.052 (5)
O71—Cr7	1.995 (5)	O83—Ni9	2.028 (5)
O10—Cr7	1.936 (5)	O80—Ni9	2.025 (5)
O73—Cr7	1.993 (5)	O12—Ni9	2.024 (5)
O10—Cr8	1.921 (5)	O13—Ni10	2.045 (5)
O11—Cr8	1.977 (5)	O89—Ni10	2.135 (5)
O72—Cr8	1.976 (5)	O91—Ni10	2.008 (5)
O74—Cr8	1.987 (5)	O93—Ni10	2.015 (5)

O75—Cr8	1.999 (5)	O15—Ni11	2.249 (5)
O77—Cr8	1.954 (5)	O16—Ni11	2.071 (5)
O11—Cr9	2.013 (5)	O108—Ni11	2.043 (5)
O12—Cr9	1.951 (5)	O109—Ni11	2.119 (6)
O76—Cr9	1.990 (5)	O110—Ni11	2.099 (5)
O78—Cr9	1.982 (5)	O111—Ni11	2.032 (5)
O79—Cr9	1.959 (5)	O104—Ni12	2.026 (6)
O81—Cr9	1.961 (5)	O106—Ni12	2.004 (6)
O13—Cr10	1.964 (5)	O107—Ni12	1.997 (5)
O14—Cr10	1.927 (5)	O16—Ni12	2.032 (5)
O92—Cr10	1.989 (5)	Ni1—N2	2.072 (6)
O94—Cr10	1.962 (5)	Ni1—N4	2.110 (7)
O95—Cr10	2.006 (5)	Ni3—N7	2.120 (7)
O97—Cr10	1.983 (5)	Ni3—N5	2.154 (6)
O14—Cr11	1.922 (5)	Ni4—N6	2.084 (6)
O96—Cr11	1.973 (5)	Ni4—N8	2.115 (7)
O98—Cr11	1.985 (5)	Ni6—N11	2.131 (6)
O99—Cr11	1.957 (5)	Ni6—N9	2.173 (6)
O15—Cr11	1.989 (5)	Ni7—N10	2.090 (6)
O101—Cr11	1.994 (5)	Ni7—N12	2.112 (7)
O15—Cr12	2.005 (5)	Ni9—N15	2.134 (6)
O100—Cr12	1.974 (6)	Ni9—N13	2.150 (6)
O102—Cr12	1.994 (6)	Ni10—N14	2.068 (6)
O103—Cr12	1.968 (6)	Ni10—N16	2.091 (6)
O105—Cr12	1.945 (7)	Ni12—N1	2.168 (6)
O16—Cr12	1.963 (5)	Ni12—N3	2.133 (6)

3. Magnetism

The magnetic susceptibility measurements were performed on polycrystalline samples with the use of a Quantum Design SQUID magnetometer MPMS-7 under an applied field of 0.1 T. Magnetization measurements were performed under external magnetic fields up to 7 T. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

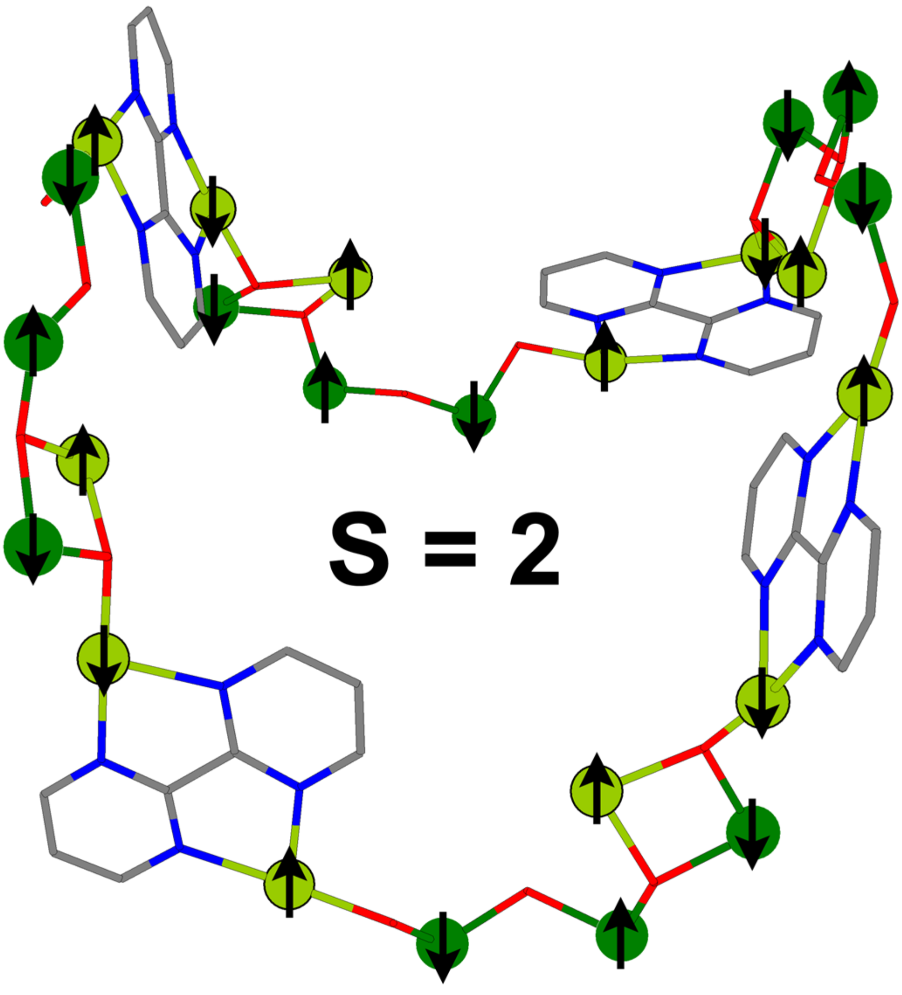

Figure S5. Possible spin topology of complex **2**.[9] Light-Green (Ni), Dark-Green (Cr), Grey (C), Red (O), Blue (N). [9]

References:

1 P. F. H. Schwab, F. Fleischer and J. Michl, *J. Org. Chem.* 2002, **67**, 443–449.

2 R. A. Coxall, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *Journal of Solid State Chemistry* 2001, **159**, 321–327.

3 G. Aromí, A. S. Batsanov, P. Christian, M. Helliwell, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *Chem. Eur. J.* 2003, **9**, 5142–5161.

4 G. Chaboussant, R. Basler, H.-U. Gudel, S. Ochsenbein, A. Parkin, S. Parsons, G. Rajaraman, A. Sieber, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *Dalton Trans.* 2004, 2758–2766.

5 SADABS, Bruker–Siemens Area Detector Absorption and Other Correction, G.M. Sheldrick, University of Göttingen, Germany, 2006, Version 2008/1.

6 PLATON; Spek, A.L., *J.Appl.Cryst.* 2003, **36**, 7-13.

7 ShelXTL 6.14 Bruker AXS Inc., Madison, WI, USA 2003.

8 ShelXL2012, G. M. Sheldrick, University of Göttingen, Germany, 2012.

9 a) J. K. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* 1991, **113**, 3012; b) A. K. Boudalis, N. Lalioti, G. A. Spoyroulias, C. P. Raptopoulou, A. Terzis, A. Bousseksou, V. Tangoulis, J.-P. Tuchagues, S. P. Perlepes, *Inorg. Chem.* 2002, **41**, 6474; c) J. Overgaard, D. E. Hibbs, E. Rentschler, G. A. Timco, F. K. Larsen, *Inorg. Chem*. 2003, **42**, 7593.