Supporting Information for

A Multiconfigurational Approach to the Electronic Structure of Trichromium Extended Metal Atom Chains.

Mariano Spivak,[1] Vaida Arcisauskaite,[2] Xavier Lopez,[1] John E. McGrady,[2] and Coen de Graaf[1,3]

[1]Departament de Quimica Fisica i Inorgànica, Universitat Rovira i Virgili, Marcellı Domingo s/n, E-43007 Tarragona, Spain.

[2]Departmentof Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR,U.K.

[3]ICREA, Passeig Lluis Companys 23, 08010, Barcelona, Spain.

Table of contents:

Table S1: Coordinates (Å) for the DFT minimum of $Cr_3(dpa)_4(CN)_2$.
Energy = -5518.8697687 a.u.

1	Cr	0.00000	0.00000	0.00000
2	Cr	0.00000	0.00000	2.37000
3	Cr	0.00000	0.00000	-2.37000
4	N	0.00000	0.00000	5.73950
5	C	0.00000	0.00000	4.55587
6	N	0.00000	0.00000	-5.73950
7	C	0.00000	0.00000	-4.55587
8	N	0.00000	2.03817	0.00000
9	N	0.00000	-2.03817	0.00000
10	N	-2.03817	0.00000	0.00000
11	N	2.03817	0.00000	0.00000
12	N	0.73701	-1.98043	2.21338
13	N	-1.98043	-0.73701	2.21338
14	N	1.98043	0.73701	2.21338
15	N	-0.73701	1.98043	2.21338
16	N	-0.73701	-1.98043	-2.21338
17	N	1.98043	-0.73701	-2.21338
18	N	-1.98043	0.73701	-2.21338
19	N	0.73701	1.98043	-2.21338
20	C	0.62344	-2.68940	1.03751
21	C	-2.68940	-0.62344	1.03751
22	C	2.68940	0.62344	1.03751
23	C	-0.62344	2.68940	1.03751
24	C	-0.62344	-2.68940	-1.03751
25	C	2.68940	-0.62344	-1.03751
26	C	-2.68940	0.62344	-1.03751
27	C	0.62344	2.68940	-1.03751
28	C	1.22663	-3.97888	0.93215
29	C	-3.97888	-1.22663	0.93215
30	C	3.97888	1.22663	0.93215
31	C	-1.22663	3.97888	0.93215
32	C	-1.22663	-3.97888	-0.93215
33	C	3.97888	-1.22663	-0.93215
34	C	-3.97888	1.22663	-0.93215
35	C	1.22663	3.97888	-0.93215
36	C	1.88870	-4.53349	2.02530
37	C	-4.53349	-1.88870	2.02530
38	C	4.53349	1.88870	2.02530
39	C	-1.88870	4.53349	2.02530
40	C	-1.88870	-4.53349	-2.02530
41	C	4.53349	-1.88870	-2.02530
42	C	-4.53349	1.88870	-2.02530
43	C	1.88870	4.53349	-2.02530
44	C	1.96335	-3.80768	3.23241

45	C	-3.80768	-1.96335	3.23241
46	C	3.80768	1.96335	3.23241
47	C	-1.96335	3.80768	3.23241
48	C	-1.96335	-3.80768	-3.23241
49	C	3.80768	-1.96335	-3.23241
50	C	-3.80768	1.96335	-3.23241
51	C	1.96335	3.80768	-3.23241
52	C	1.38568	-2.53764	3.26871
53	C	-2.53764	-1.38568	3.26871
54	C	2.53764	1.38568	3.26871
55	C	-1.38568	2.53764	3.26871
56	C	-1.38568	-2.53764	-3.26871
57	C	2.53764	-1.38568	-3.26871
58	C	-2.53764	1.38568	-3.26871
59	C	1.38568	2.53764	-3.26871
60	H	1.19504	-4.50690	-0.03088
61	H	-4.50690	-1.19504	-0.03088
62	H	4.50690	1.19504	-0.03088
63	H	-1.19504	4.50690	-0.03088
64	H	-1.19504	-4.50690	0.03088
65	H	4.50690	-1.19504	0.03088
66	H	-4.50690	1.19504	0.03088
67	H	1.19504	4.50690	0.03088
68	H	2.36445	-5.52335	1.93420
69	H	-5.52335	-2.36445	1.93420
70	H	5.52335	2.36445	1.93420
71	H	-2.36445	5.52335	1.93420
72	H	-2.36445	-5.52335	-1.93420
73	H	5.52335	-2.36445	-1.93420
74	H	-5.52335	2.36445	-1.93420
75	H	2.36445	5.52335	-1.93420
76	H	2.46843	-4.20693	4.12329
77	H	-4.20693	-2.46843	4.12329
78	H	4.20693	2.46843	4.12329
79	H	-2.46843	4.20693	4.12329
80	H	-2.46843	-4.20693	-4.12329
81	H	4.20693	-2.46843	-4.12329
82	H	-4.20693	2.46843	-4.12329
83	H	2.46843	4.20693	-4.12329
84	H	1.41444	-1.91533	4.17756
85	H	-1.91533	-1.41444	4.17756
86	H	1.91533	1.41444	4.17756
87	H	-1.41444	1.91533	4.17756
88	H	-1.41444	-1.91533	-4.17756
89	H	1.91533	-1.41444	-4.17756
90	H	-1.91533	1.41444	-4.17756

91	H	1.41444	1.91533	-4.17756

Table S2: Coordinates (Å) for the DFT minimum of $Cr_3(dpa)_4(NCS)_2$.
Energy = -6315.1954328 a.u.

1	Cr	0.00000	0.00000	0.00173
2	Cr	0.00000	0.00000	2.37073
3	Cr	0.00000	0.00000	-2.36728
4	N	0.00000	0.00000	4.47523
5	C	0.00000	0.00000	5.68356
6	S	-0.00001	-0.00003	7.30106
7	N	0.00000	0.00000	-4.47184
8	C	0.00000	-0.00001	-5.68017
9	S	0.00005	0.00006	-7.29767
10	N	0.00006	2.03903	0.00170
11	N	-0.00006	-2.03903	0.00171
12	N	-2.03903	0.00006	0.00171
13	N	2.03903	-0.00006	0.00171
14	N	0.74075	-1.97561	2.21280
15	N	-1.97561	-0.74075	2.21280
16	N	1.97561	0.74075	2.21280
17	N	-0.74075	1.97561	2.21280
18	N	-0.74090	-1.97555	-2.20937
19	N	1.97555	-0.74090	-2.20938
20	N	-1.97555	0.74090	-2.20938
21	N	0.74090	1.97555	-2.20938
22	C	0.62290	-2.68916	1.04009
23	C	-2.68916	-0.62290	1.04009
24	C	2.68916	0.62290	1.04009
25	C	-0.62290	2.68916	1.04009
26	C	-0.62312	-2.68910	-1.03666
27	C	2.68910	-0.62312	-1.03666
28	C	-2.68910	0.62312	-1.03666
29	C	0.62312	2.68910	-1.03667
30	C	1.22284	-3.98060	0.94022
31	C	-3.98060	-1.22284	0.94022
32	C	3.98060	1.22284	0.94021
33	C	-1.22284	3.98060	0.94021
34	C	-1.22320	-3.98048	-0.93677
35	C	3.98048	-1.22320	-0.93677
36	C	-3.98048	1.22319	-0.93677
37	C	1.22319	3.98047	-0.93677
38	C	1.88678	-4.53085	2.03451
39	C	-4.53085	-1.88677	2.03451
40	C	4.53085	1.88678	2.03451
41	C	-1.88677	4.53086	2.03451

42	C	-1.88720	-4.53066	-2.03105
43	C	4.53066	-1.88720	-2.03106
44	C	-4.53066	1.88720	-2.03106
45	C	1.88720	4.53066	-2.03106
46	C	1.96874	-3.79826	3.23717
47	C	-3.79826	-1.96874	3.23718
48	C	3.79826	1.96874	3.23717
49	C	-1.96874	3.79826	3.23717
50	C	-1.96910	-3.79808	-3.23372
51	C	3.79807	-1.96910	-3.23372
52	C	-3.79808	1.96909	-3.23372
53	C	1.96909	3.79807	-3.23373
54	C	1.39404	-2.52686	3.26772
55	C	-2.52686	-1.39404	3.26772
56	C	2.52687	1.39404	3.26772
57	C	-1.39404	2.52687	3.26772
58	C	-1.39426	-2.52674	-3.26429
59	C	2.52674	-1.39426	-3.26429
60	C	-2.52674	1.39425	-3.26429
61	C	1.39425	2.52674	-3.26429
62	H	1.18821	-4.51397	-0.01972
63	H	-4.51397	-1.18821	-0.01972
64	H	4.51397	1.18821	-0.01973
65	H	-1.18821	4.51397	-0.01972
66	H	-1.18862	-4.51383	0.02318
67	H	4.51383	-1.18862	0.02317
68	H	-4.51383	1.18862	0.02317
69	H	1.18862	4.51383	0.02317
70	H	2.35977	-5.52233	1.94732
71	H	-5.52233	-2.35977	1.94732
72	H	5.52233	2.35977	1.94731
73	H	-2.35977	5.52234	1.94731
74	H	-2.36031	-5.52209	-1.94384
75	H	5.52209	-2.36031	-1.94384
76	H	-5.52209	2.36031	-1.94384
77	H	2.36031	5.52209	-1.94385
78	H	2.47857	-4.19298	4.12736
79	H	-4.19298	-2.47856	4.12736
80	H	4.19298	2.47857	4.12735
81	H	-2.47856	4.19298	4.12736
82	H	-2.47897	-4.19275	-4.12390
83	H	4.19275	-2.47897	-4.12390
84	H	-4.19275	2.47897	-4.12390
85	H	2.47897	4.19275	-4.12390
86	H	1.43319	-1.89621	4.16899
87	H	-1.89621	-1.43319	4.16899

88	H	1.89621	1.43319	4.16899
89	H	-1.43319	1.89621	4.16899
90	H	-1.43334	-1.89609	-4.16556
91	H	1.89609	-1.43334	-4.16556
92	H	-1.89609	1.43334	-4.16556
93	H	1.43334	1.89609	-4.16557

Table S3: Coordinates (Å) for the DFT minimum of $Cr_3(dpa)_4(NO_3)_2$.
Energy = -5893.6334119 a.u.

1	Cr	0.03500	0.03451	0.01453
2	Cr	0.03873	0.01495	2.34445
3	Cr	0.01514	0.03798	-2.31538
4	O	-1.40161	-0.29759	-5.99972
5	O	0.54822	-1.29646	-5.91125
6	N	-0.28303	-0.47027	-5.49290
7	O	0.04615	0.26319	-4.44290
8	O	0.26356	0.04580	4.47180
9	N	-0.47249	-0.27578	5.52232
10	O	-1.28885	0.56440	5.94205
11	O	-0.31200	-1.39662	6.02823
12	N	-0.82166	-1.88866	-2.18334
13	N	-1.88455	0.94186	-2.17225
14	N	1.90881	-0.86410	-2.23898
15	N	0.90438	1.95161	-2.18990
16	N	-1.39219	1.48800	0.04230
17	N	-1.41754	-1.40088	0.01538
18	N	1.47171	-1.40965	-0.01270
19	N	1.48521	1.46769	0.01452
20	N	-1.89791	-0.79808	2.21366
21	N	0.92015	-1.89518	2.20184
22	N	-0.84071	1.91961	2.26811
23	N	1.96275	0.88092	2.21858
24	C	-0.69141	-2.75931	-3.21794
25	C	-1.18811	-4.06316	-3.18900
26	C	-1.81714	-4.50588	-2.00742
27	C	-1.93141	-3.63713	-0.92400
28	C	-1.43433	-2.30385	-1.02005
29	C	-2.32065	-1.40630	1.05087
30	C	-3.65983	-1.88743	0.95543
31	C	-4.52701	-1.76151	2.03885
32	C	-4.07650	-1.13695	3.21989
33	C	-2.76661	-0.65641	3.24832
34	C	2.71814	-0.83973	-3.32968
35	C	4.01737	-1.34997	-3.32426
36	C	4.51285	-1.88804	-2.11854

37	C	3.68898	-1.93342	-0.99516
38	C	2.35318	-1.43882	-1.06819
39	C	1.49870	-2.31416	1.02343
40	C	1.99000	-3.64888	0.91702
41	C	1.92981	-4.50492	2.01505
42	C	1.37844	-4.04134	3.22676
43	C	0.87705	-2.73867	3.26714
44	C	2.81138	0.79308	3.27473
45	C	4.11831	1.28200	3.24891
46	C	4.58245	1.86544	2.05157
47	C	3.72610	1.96010	0.95647
48	C	2.38732	1.47597	1.05117
49	C	1.50412	2.36936	-1.02236
50	C	2.00390	3.70236	-0.92761
51	C	1.92027	4.55949	-2.02297
52	C	1.33220	4.10195	-3.22058
53	C	0.82748	2.80101	-3.24633
54	C	-2.72873	0.90887	-3.23737
55	C	-4.02555	1.42518	-3.19656
56	C	-4.48272	1.98100	-1.98445
57	C	-3.62585	2.03091	-0.88655
58	C	-2.29669	1.52494	-0.99359
59	C	-1.41106	2.37006	1.09754
60	C	-1.89070	3.71131	1.02441
61	C	-1.83465	4.53523	2.14727
62	C	-1.30082	4.03433	3.35264
63	C	-0.80579	2.72927	3.35826
64	H	-0.13918	-2.39521	-4.09916
65	H	-1.06088	-4.71588	-4.06393
66	H	-2.35877	-3.98192	0.02755
67	H	-4.00982	-2.31184	0.00446
68	H	-4.72749	-1.00108	4.09480
69	H	-2.39528	-0.10843	4.12916
70	H	0.43384	-2.33025	4.19198
71	H	1.31989	-4.67570	4.12248
72	H	2.38011	-4.00050	-0.04801
73	H	4.06597	-2.31753	-0.03725
74	H	4.62463	-1.31338	-4.23964
75	H	2.26283	-0.41106	-4.23614
76	H	0.34073	2.37972	-4.14029
77	H	1.24752	4.74267	-4.10972
78	H	2.41525	4.05323	0.02883
79	H	4.08157	2.36825	0.00036
80	H	4.75825	1.18912	4.13781
81	H	2.38425	0.31110	4.16850
82	H	-0.38165	2.26932	4.26451

83	H	-1.25612	4.64168	4.26760
84	H	-2.27182	4.09217	0.06683
85	H	-3.97301	2.42393	0.07889
86	H	-4.66070	1.37430	-4.09218
87	H	-2.32569	0.46114	-4.16234
88	H	5.54798	-2.26056	-2.05351
89	H	2.29752	-5.53981	1.92360
90	H	-2.19554	5.57446	2.08211
91	H	-5.51344	2.36015	-1.89257
92	H	2.29405	5.59282	-1.93990
93	H	-5.56493	-2.12187	1.95493
94	H	-2.18992	-5.53938	-1.92299
95	H	5.62008	2.22708	1.96851

Table S4: Coordinates (Å) for the CASPT2 minimum of $Cr_3(dpa)_4(CN)_2$. Energy = -5518.8693672 a.u.

1	C	0.00000	0.00000	0.00000
2	C	0.00000	0.00000	2.42000
3	C	0.00000	0.00000	-2.42000
4	N	0.00000	0.00000	5.87123
5	C	0.00000	0.00000	4.69827
6	N	0.00000	0.00000	-5.87123
7	C	0.00000	0.00000	-4.69827
8	N	0.00000	2.05705	0.00000
9	N	-2.05705	0.00000	0.00000
10	N	0.74042	-1.99585	2.20608
11	N	-1.99585	-0.74042	2.20608
12	N	-0.74042	-1.99585	-2.20608
13	N	1.99585	-0.74042	-2.20608
14	N	0.00000	-2.05705	0.00000
15	N	2.05705	0.00000	0.00000
16	N	-0.74042	1.99585	2.20608
17	N	1.99585	0.74042	2.20608
18	N	0.74042	1.99585	-2.20608
19	N	-1.99585	0.74042	-2.20608
20	C	0.61379	-2.70759	1.03885
21	C	-2.70759	-0.61379	1.03885
22	C	-0.61379	-2.70759	-1.03885
23	C	2.70759	-0.61379	-1.03885
24	C	1.19329	-3.99806	0.94375
25	C	-3.99806	-1.19329	0.94375
26	C	-1.19329	-3.99806	-0.94375
27	C	3.99806	-1.19329	-0.94375
28	C	1.86278	-4.54821	2.02142
29	C	-4.54821	-1.86278	2.02142

30	C	-1.86278	-4.54821	-2.02142
31	C	4.54821	-1.86278	-2.02142
32	C	1.97010	-3.81574	3.21334
33	C	-3.81574	-1.97010	3.21334
34	C	-1.97010	-3.81574	-3.21334
35	C	3.81574	-1.97010	-3.21334
36	C	1.40747	-2.55202	3.24697
37	C	-2.55202	-1.40747	3.24697
38	C	-1.40747	-2.55202	-3.24697
39	C	2.55202	-1.40747	-3.24697
40	C	-0.61379	2.70759	1.03885
41	C	2.70759	0.61379	1.03885
42	C	0.61379	2.70759	-1.03885
43	C	-2.70759	0.61379	-1.03885
44	C	-1.19329	3.99806	0.94375
45	C	3.99806	1.19329	0.94375
46	C	1.19329	3.99806	-0.94375
47	C	-3.99806	1.19329	-0.94375
48	C	-1.86278	4.54821	2.02142
49	C	4.54821	1.86278	2.02142
50	C	1.86278	4.54821	-2.02142
51	C	-4.54821	1.86278	-2.02142
52	C	-1.97010	3.81574	3.21334
53	C	3.81574	1.97010	3.21334
54	C	1.97010	3.81574	-3.21334
55	C	-3.81574	1.97010	-3.21334
56	C	-1.40747	2.55202	3.24697
57	C	2.55202	1.40747	3.24697
58	C	1.40747	2.55202	-3.24697
59	C	-2.55202	1.40747	-3.24697
60	H	1.13894	-4.53534	0.00060
61	H	-4.53534	-1.13894	0.00060
62	H	-1.13894	-4.53534	-0.00060
63	H	4.53534	-1.13894	-0.00060
64	H	2.31730	-5.53407	1.93118
65	H	-5.53407	-2.31730	1.93118
66	H	-2.31730	-5.53407	-1.93118
67	H	5.53407	-2.31730	-1.93118
68	H	2.48802	-4.20705	4.08551
69	H	-4.20705	-2.48802	4.08551
70	H	-2.48802	-4.20705	-4.08551
71	H	4.20705	-2.48802	-4.08551
72	H	1.47362	-1.93424	4.14011
73	H	-1.93424	-1.47362	4.14011
74	H	-1.47362	-1.93424	-4.14011
75	H	1.93424	-1.47362	-4.14011

76	H	-1.13894	4.53534	0.00060
77	H	4.53534	1.13894	0.00060
78	H	1.13894	4.53534	-0.00060
79	H	-4.53534	1.13894	-0.00060
80	H	-2.31730	5.53407	1.93118
81	H	5.53407	2.31730	1.93118
82	H	2.31730	5.53407	-1.93118
83	H	-5.53407	2.31730	-1.93118
84	H	-2.48802	4.20705	4.08551
85	H	4.20705	2.48802	4.08551
86	H	2.48802	4.20705	-4.08551
87	H	-4.20705	2.48802	-4.08551
88	H	-1.47362	1.93424	4.14011
89	H	1.93424	1.47362	4.14011
90	H	1.47362	1.93424	-4.14011
91	H	-1.93424	1.47362	-4.14011

Table S5: Coordinates (Å) for the CASPT2 minimum of $Cr_3(dpa)_4(NCS)_2$. Energy = -6315.1950103 a.u.

1	Cr	0.00000	0.00000	0.00000
2	Cr	0.00000	0.00000	2.33000
3	Cr	0.00000	0.00000	-2.33000
4	N	0.00000	0.00000	4.56342
5	C	0.00000	0.00000	5.75503
6	S	0.00000	0.00000	7.43283
7	N	0.00000	0.00000	-4.56342
8	C	0.00000	0.00000	-5.75503
9	S	0.00000	0.00000	-7.43283
10	N	0.00000	2.06289	0.00000
11	N	-2.06289	0.00000	0.00000
12	N	0.76666	-1.98501	2.18777
13	N	-0.76666	-1.98501	-2.18777
14	N	-1.98501	-0.76666	2.18777
15	N	1.98501	-0.76666	-2.18777
16	C	0.63101	-2.71814	1.03407
17	C	-0.63101	-2.71814	-1.03407
18	C	-2.71814	-0.63101	1.03407
19	C	2.71814	-0.63101	-1.03407
20	C	1.21461	-4.01859	0.94982
21	C	-1.21461	-4.01859	-0.94982
22	C	-4.01859	-1.21461	0.94982
23	C	4.01859	-1.21461	-0.94982
24	C	1.89574	-4.54866	2.04431
25	C	-1.89574	-4.54866	-2.04431
26	C	-4.54866	-1.89574	2.04431

27	C	4.54866	-1.89574	-2.04431
28	C	2.00712	-3.78813	3.22972
29	C	-2.00712	-3.78813	-3.22972
30	C	-3.78813	-2.00712	3.22972
31	C	3.78813	-2.00712	-3.22972
32	C	1.43832	-2.51351	3.24150
33	C	-1.43832	-2.51351	-3.24150
34	C	-2.51351	-1.43832	3.24150
35	C	2.51351	-1.43832	-3.24150
36	H	1.16064	-4.56661	0.01689
37	H	-1.16064	-4.56661	-0.01689
38	H	-4.56661	-1.16064	0.01689
39	H	4.56661	-1.16064	-0.01689
40	H	2.35080	-5.53378	1.97429
41	H	-2.35080	-5.53378	-1.97429
42	H	-5.53378	-2.35080	1.97429
43	H	5.53378	-2.35080	-1.97429
44	H	2.52267	-4.16154	4.10753
45	H	-2.52267	-4.16154	-4.10753
46	H	-4.16154	-2.52267	4.10753
47	H	4.16154	-2.52267	-4.10753
48	H	1.49836	-1.88237	4.12178
49	H	-1.49836	-1.88237	-4.12178
50	H	-1.88237	-1.49836	4.12178
51	H	1.88237	-1.49836	-4.12178
52	N	0.00000	-2.06289	0.00000
53	N	2.06289	0.00000	0.00000
54	N	-0.76666	1.98501	2.18777
55	N	0.76666	1.98501	-2.18777
56	N	1.98501	0.76666	2.18777
57	N	-1.98501	0.76666	-2.18777
58	C	-0.63101	2.71814	1.03407
59	C	0.63101	2.71814	-1.03407
60	C	2.71814	0.63101	1.03407
61	C	-2.71814	0.63101	-1.03407
62	C	-1.21461	4.01859	0.94982
63	C	1.21461	4.01859	-0.94982
64	C	4.01859	1.21461	0.94982
65	C	-4.01859	1.21461	-0.94982
66	C	-1.89574	4.54866	2.04431
67	C	1.89574	4.54866	-2.04431
68	C	4.54866	1.89574	2.04431
69	C	-4.54866	1.89574	-2.04431
70	C	-2.00712	3.78813	3.22972
71	C	2.00712	3.78813	-3.22972
72	C	3.78813	2.00712	3.22972

73	C	-3.78813	2.00712	-3.22972
74	C	-1.43832	2.51351	3.24150
75	C	1.43832	2.51351	-3.24150
76	C	2.51351	1.43832	3.24150
77	C	-2.51351	1.43832	-3.24150
78	H	-1.16064	4.56661	0.01689
79	H	1.16064	4.56661	-0.01689
80	H	4.56661	1.16064	0.01689
81	H	-4.56661	1.16064	-0.01689
82	H	-2.35080	5.53378	1.97429
83	H	2.35080	5.53378	-1.97429
84	H	5.53378	2.35080	1.97429
85	H	-5.53378	2.35080	-1.97429
86	H	-2.52267	4.16154	4.10753
87	H	2.52267	4.16154	-4.10753
88	H	4.16154	2.52267	4.10753
89	H	-4.16154	2.52267	-4.10753
90	H	-1.49836	1.88237	4.12178
91	H	1.49836	1.88237	-4.12178
92	H	1.88237	1.49836	4.12178
93	H	-1.88237	1.49836	-4.12178

Table S6: Coordinates (Å) for the CASPT2 minimum of $Cr_3(dpa)_4(NO_3)_2$. Energy = -5893.6324603 a.u.

1	Cr	0.00000	0.00000	0.18770
2	Cr	0.00000	0.00000	2.13770
3	Cr	0.00000	0.00000	-2.45230
4	O	-0.18946	-1.08198	6.47803
5	N	0.00000	0.00000	5.86139
6	O	0.00000	0.00000	4.57880
7	O	0.18946	1.08198	6.47803
8	O	0.00000	0.00000	-4.70125
9	O	-1.06450	0.27148	-6.60111
10	N	0.00000	0.00000	-5.99316
11	O	1.06450	-0.27148	-6.60111
12	N	-0.59002	1.96403	-0.02243
13	N	-1.96406	-0.58699	-0.02054
14	N	1.18620	-1.73804	2.19430
15	N	-1.73651	-1.18383	2.19684
16	N	-0.11431	-2.09757	-2.24462
17	N	2.09979	-0.10380	-2.24888
18	N	0.59002	-1.96403	-0.02243
19	N	1.96406	0.58699	-0.02054

20	N	-1.18620	1.73804	2.19430
21	N	1.73651	1.18383	2.19684
22	N	0.11431	2.09757	-2.24462
23	N	-2.09979	0.10380	-2.24888
24	C	1.31347	-2.45708	1.03574
25	C	-2.45854	-1.30723	1.03937
26	C	0.18871	-2.74719	-1.07665
27	C	2.74705	0.18582	-1.07595
28	C	2.20821	-3.55173	0.98626
29	C	-3.55742	-2.19674	0.99313
30	C	-0.01094	-4.14812	-0.99454
31	C	4.14615	-0.02383	-0.98968
32	C	2.92061	-3.91470	2.11624
33	C	-3.92063	-2.90712	2.12448
34	C	-0.47068	-4.85726	-2.08868
35	C	4.85742	-0.47569	-2.08599
36	C	2.75277	-3.18916	3.30522
37	C	-3.19033	-2.74391	3.31150
38	C	-0.75055	-4.17957	-3.28502
39	C	4.18349	-0.73236	-3.28947
40	C	1.89014	-2.10673	3.28983
41	C	-2.10330	-1.88725	3.29450
42	C	-0.57398	-2.80889	-3.30367
43	C	2.81332	-0.54746	-3.31392
44	C	-1.31347	2.45708	1.03574
45	C	2.45854	1.30723	1.03937
46	C	-0.18871	2.74719	-1.07665
47	C	-2.74705	-0.18582	-1.07595
48	C	-2.20821	3.55173	0.98626
49	C	3.55742	2.19674	0.99313
50	C	0.01094	4.14812	-0.99454
51	C	-4.14615	0.02383	-0.98968
52	C	-2.92061	3.91470	2.11624
53	C	3.92063	2.90712	2.12448
54	C	0.47068	4.85726	-2.08868
55	C	-4.85742	0.47569	-2.08599
56	C	-2.75277	3.18916	3.30522
57	C	3.19033	2.74391	3.31150
58	C	0.75055	4.17957	-3.28502
59	C	-4.18349	0.73236	-3.28947
60	C	-1.89014	2.10673	3.28983
61	C	2.10330	1.88725	3.29450
62	C	0.57398	2.80889	-3.30367
63	C	-2.81332	0.54746	-3.31392
64	H	2.35519	-4.08139	0.04903
65	H	-4.09061	-2.34147	0.05751

66	H	0.16680	-4.65620	-0.05069
67	H	4.65072	0.14124	-0.04159
68	H	3.61855	-4.74959	2.06988
69	H	-4.75857	-3.60160	2.08037
70	H	-0.63173	-5.93126	-2.00768
71	H	5.93004	-0.64551	-2.00187
72	H	3.29329	-3.44351	4.21309
73	H	-3.44603	-3.28394	4.21971
74	H	-1.11385	-4.69660	-4.16919
75	H	4.70419	-1.08261	-4.17690
76	H	1.73097	-1.49190	4.17196
77	H	-1.47919	-1.73482	4.17284
78	H	-0.79968	-2.22581	-4.19391
79	H	2.23213	-0.74120	-4.21398
80	H	-2.35519	4.08139	0.04903
81	H	4.09061	2.34147	0.05751
82	H	-0.16680	4.65620	-0.05069
83	H	-4.65072	-0.14124	-0.04159
84	H	-3.61855	4.74959	2.06988
85	H	4.75857	3.60160	2.08037
86	H	0.63173	5.93126	-2.00768
87	H	-5.93004	0.64551	-2.00187
88	H	-3.29329	3.44351	4.21309
89	H	3.44603	3.28394	4.21971
90	H	1.11385	4.69660	-4.16919
91	H	-4.70419	1.08261	-4.17690
92	H	-1.73097	1.49190	4.17196
93	H	1.47919	1.73482	4.17284
94	H	0.79968	2.22581	-4.19391
95	H	-2.23213	0.74120	-4.21398

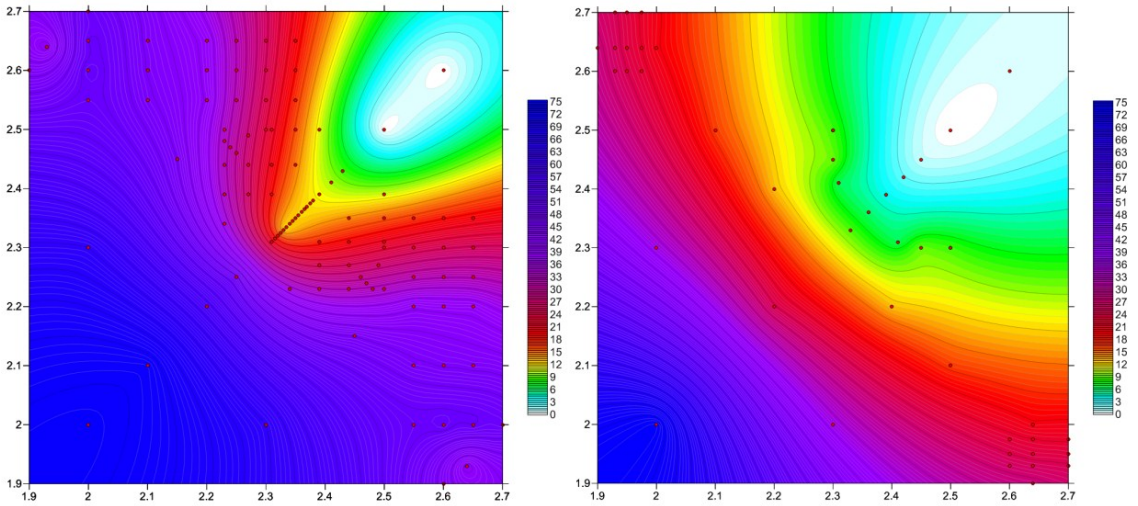

Figure S1: Potential Energy Surface (kcal/mol) at CASSCF(12,12) level for $Cr_3(dpa)_4(NCS)_2$ (left) and $Cr_3(dpa)_4(NO_3)_2$ (right)

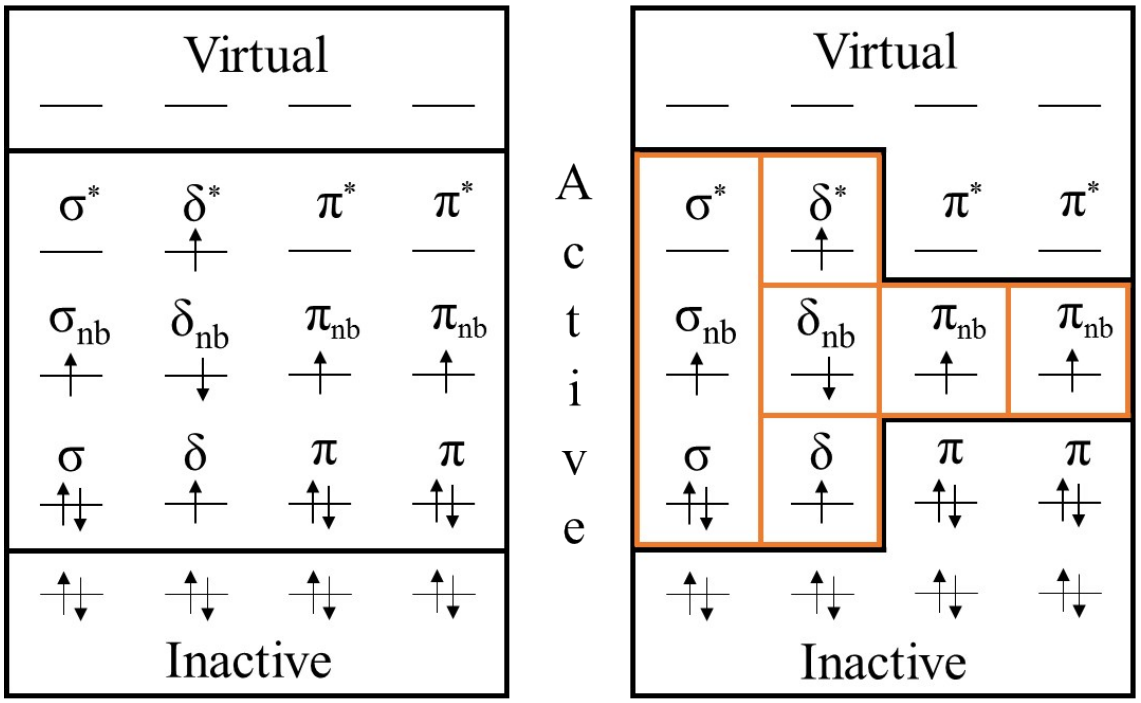

Figure S2: Scheme of the CAS(12,12) orbitals (left) and the subdivision of the active space with the GAS formalism (right). Each GAS subspace represented with the orange contour.

As mentioned in the main article, the use of the conventional CASSCF method generates a large number of configuration state functions (CSFs) with negligible contributions to the wave function. Figure S1 (left) shows a scheme of the active space with occupations that correspond to one of the most important CSF for the ground state

(i. e. $(\sigma)^2(\sigma_{nb})^1(\sigma^*)^0(\delta)^1(\delta_{nb})^1(\delta^*)^1\{(\pi)^2(\pi_{nb})^1(\pi^*)^0\}_{x,y}$). In order to focus our analysis in the σ manifold, we use GASSCF to freeze the occupations of the δ and π orbitals to those of the aforementioned CSF. Figure S1 (right) presents the active space resulting from the GASSCF, where we can see that: i) the π and π^* orbitals are now out of the active space, in the inactive (doubly occupied) and virtual (empty) spaces respectively. ii) the three σ orbitals are included in the same GAS subspace which contains exactly three electrons. iii) the five remaining orbitals (δ, δ_{nb}, δ^*, $\{\pi_{nb}\}_{x,y}$) are separated on five subspaces with one electron each. The space of configurations is reduced greatly from 98425 CSFs in CAS to 50 CSFs in GAS, for the quintet (S = 2) total spin. However, each of the σ manifold arrangements ($(\sigma)^A(\sigma_{nb})^B(\sigma^*)^C$, $A + B + C = 3$) is still split into 5 different CSFs due to the couplings of the δ and π manifolds. Since the local spin of each GAS subspace cannot be forced, in order to reduce each arrangement to a single CSF we calculated the septet (S = 3) spin state, which correspond to the change of spin of the electron in the δ_{nb} orbital in Figure S1 (right). The number of CSFs is reduced to 13 and we take the eight energy states that have the largest contribution from the different σ arrangements (See Table S7 for the energy and contributions of these states in the case of the symmetric CN structure). In order to minimize the differences between the wave functions of the quintet and septet states, the calculations of the septet state consisted in only the configuration interaction part without the re-optimization of the molecular orbitals of the quintet state, a procedure called CIONLY.

We can mention that we tested the results for other possible GAS configurations with similar results. For example, treating the δ and π manifolds in the same way, i.e. $(\delta)^2(\delta_{nb})^1(\delta^*)^0$, gave different absolute values for the matrix elements of the effective Hamiltonian method but ultimately the same trends were observed.

Finally, we can explain the choice of the two structures analyzed with the effective Hamiltonian: a symmetric 2.33 Å structure and a slightly unsymmetric counterpart (2.28-2.38 Å). The idea is to study the effect breaking the symmetry of chain produces and as such, the starting point (symmetric structure) was not very important but the comparison with the distorted structure was. Then, to compare between axial ligands we needed to isolate the effect of the Cr-Cr distances and we selected the structure with 2.33 Å distances as a reference for all the compounds. We are not comparing between structures of minimum energy, which would for example be the 1.95-2.64 Å for NO_3, because the highly unsymmetric structures cannot be compared with the symmetric ones, as they have different (localized) molecular orbitals.

Table S7: GASSCF states and CI coefficients from the selected CSFs for CN symmetric structure (2.33 Å). States 3, 4, 5, 8 and 11 are not a local doublet in the sigma manifold.

State	1	2	6	7	9	10	12	13
E (eV)	0.0	1.	12.9	14.0	16.9	17.0	21.	22
1	-0.841	0.	0.000	0.357	0.000	-0.378	0.	-0
2	-0.210	0.	0.000	0.409	-0.001	0.855	0.	-0
3	0.346	0.	0.000	0.736	0.000	-0.155	0.	0
4	0.330	0.	0.000	0.401	0.000	-0.269	0.	-0
5	0.000	0.	-0.761	0.000	-0.100	0.000	0.	0
6	0.000	0.	0.510	0.000	-0.585	-0.001	-0.	0
7	0.000	-0.	-0.400	0.000	-0.539	0.000	-0.	0
8	0.000	-0.	-0.010	0.000	-0.598	0.000	0.	0

Table S8: Effective Hamiltonian for CN symmetric structure (2.33 Å).

CSFs	1	2	3	4	5	6	7	8
1	0.00	4.13	-3.44	4.57	0.00	0.00	0.00	0.00
2	4.13	10.63	-0.17	-5.25	0.00	0.00	0.00	0.00
3	-3.44	-0.17	11.54	1.46	0.00	0.00	0.00	0.00
4	4.57	-5.25	1.46	13.79	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	4.96	-4.22	1.37	4.16
6	0.00	0.00	0.00	0.00	-4.22	5.94	4.61	2.98
7	0.00	0.00	0.00	0.00	1.37	4.61	11.94	-4.22
8	0.00	0.00	0.00	0.00	4.16	2.98	-4.22	12.71

Eigenvalues after diagonalization: -4.32; -2.74; 8.58; 9.70; 12.53; 12.65; 17.23; 17.99

Table S9: GASSCF states and CI coefficients from the selected CSFs for CN unsymmetric structure (2.28-2.38 Å). States 3, 4, 5, 8 and 11 are not a local doublet in the sigma manifold.

State	1	2	6	7	9	10	12	13
E (eV)	0.0	1.	12.7	13.8	17.0	17.1	21.	22
1	0.853	0.	-0.024	-0.342	-0.003	-0.374	-0.	0
2	0.201	-0.	-0.118	-0.401	-0.088	0.861	-0.	0
3	-0.325	0.	-0.058	-0.733	0.066	-0.161	0.	-0
4	-0.324	-0.	-0.050	-0.398	-0.083	-0.259	-0.	0
5	0.040	0.	-0.754	0.141	-0.080	0.013	-0.	0
6	0.044	0.	0.500	0.007	-0.601	0.066	0.	0
7	-0.040	-0.	-0.400	0.037	-0.536	-0.114	0.	-0
8	-0.039	-0.	-0.028	-0.021	-0.570	-0.079	-0.	-0

Table S10: Effective Hamiltonian for CN unsymmetric structure (2.28-2.38 Å).

CSFs	1	2	3	4	5	6	7	8
1	0.00	3.84	-3.38	4.58	-0.46	-0.55	0.	0
2	3.84	10.45	0.03	-5.10	-1.38	-1.31	1.	1
3	-3.38	0.03	11.63	1.18	0.63	1.10	-0.	-0
4	4.58	-5.10	1.18	14.18	0.50	0.53	-0.	-0
5	-0.46	-1.38	0.63	0.50	5.16	-4.01	1.	3
6	-0.55	-1.31	1.10	0.53	-4.01	6.34	4.	2
7	0.54	1.02	-0.62	-0.79	1.12	4.41	12.	-4
8	0.50	1.06	-0.63	-0.87	3.94	2.92	-4.	13

Eigenvalues after diagonalization: -4.09; -2.46; 8.56; 9.75; 12.87; 12.98; 17.48; 18.36

Table S11: GASSCF states and CI coefficients from the selected CSFs for NO_3 symmetric structure (2.33 Å). States 3, 4, 5, 8 and 11 are not a local doublet in the sigma manifold.

State	1	2	6	7	9	10	12	13
E (eV)	0.0	1.	13.3	14.4	16.6	16.7	21.	22
1	-0.833	0.	-0.001	0.362	-0.008	-0.380	0.	-0
2	0.211	0.	0.001	-0.417	-0.016	-0.819	-0.	0
3	-0.351	0.	0.002	-0.734	0.003	0.130	0.	-0
4	0.338	0.	-0.001	0.392	-0.006	-0.312	0.	-0
5	0.000	-0.	-0.753	-0.002	0.180	-0.003	-0.	-0
6	0.000	0.	-0.551	-0.002	-0.533	0.011	-0.	-0
7	0.000	-0.	0.356	0.001	-0.534	0.011	-0.	-0
8	0.000	0.	0.051	0.001	0.631	-0.013	-0.	-0

Table S12: Effective Hamiltonian for NO_3 symmetric structure (2.33 Å)

CSFs	1	2	3	4	5	6	7	8
1	0.00	-4.33	3.29	4.60	0.00	0.00	0.	0
2	-4.33	10.65	-0.17	5.15	0.00	0.00	0.	0
3	3.29	-0.17	11.35	-1.82	0.00	0.00	0.	0
4	4.60	5.15	-1.82	13.42	0.00	0.00	0.	0
5	0.00	0.00	0.00	0.00	5.20	4.30	-1.	4
6	0.00	0.00	0.00	0.00	4.30	5.65	4.	-2
7	0.00	0.00	0.00	0.00	-1.56	4.62	12.	4
8	0.00	0.00	0.00	0.00	4.28	-2.76	4.	12

Eigenvalues after diagonalization: -4.50; -2.95; 8.69; 9.95; 12.08; 12.21; 17.11; 17.75

Table S13: GASSCF states and CI coefficients from the selected CSFs for NO_3 unsymmetric structure (2.28-2.38 Å). States 3, 4, 5, 8 and 11 are not a local doublet in the sigma manifold.

State	1	2	6	7	9	10	12	13
E (eV)	0.0	1.	13.1	14.3	16.7	16.9	21.	22
1	-0.843	0.	0.005	0.351	0.124	-0.364	0.	0
2	0.206	0.	-0.074	-0.414	0.208	-0.825	-0.	-0
3	-0.340	-0.	-0.027	-0.736	-0.011	0.146	0.	0
4	0.330	-0.	0.017	0.392	0.144	-0.271	0.	0
5	0.025	-0.	-0.756	0.078	-0.142	-0.044	-0.	0
6	-0.028	0.	-0.536	-0.013	0.510	0.214	-0.	0
7	0.025	-0.	0.367	-0.018	0.528	0.098	-0.	0
8	-0.025	0.	0.027	-0.010	-0.602	-0.150	-0.	0

Table S14: Effective Hamiltonian for **NO_3** unsymmetric structure (2.28-2.38 Å).

CSFs	1	2	3	4	5	6	7	8
1	0.00	-4.16	3.32	4.58	0.28	-0.37	0.34	-0.32
2	-4.16	10.66	-0.11	5.13	-0.86	0.85	-0.64	0.73
3	3.32	-0.11	11.52	-1.61	0.39	-0.72	0.36	-0.39
4	4.58	5.13	-1.61	13.86	-0.32	0.33	-0.47	0.58
5	0.28	-0.86	0.39	-0.32	5.26	4.19	-1.38	4.16
6	-0.37	0.85	-0.72	0.33	4.19	5.90	4.55	-2.77
7	0.34	-0.64	0.36	-0.47	-1.38	4.55	12.32	4.19
8	-0.32	0.73	-0.39	0.58	4.16	-2.77	4.19	12.69

Eigenvalues after diagonalization: -4.31; -2.70; 8.76; 9.95; 12.41; 12.57; 17.37; 18.12

Table S15: GASSCF states and CI coefficients from the selected CSFs for NCS symmetric structure (2.33 Å). States 3, 4, 5, 8 and 11 are not a local doublet in the sigma manifold.

State	1	2	6	7	9	10	12	13
E (eV)	0.0	1.	13.1	14.2	16.8	17.0	21.	22
1	0.837	0.	0.000	0.359	0.001	-0.386	0.	-0
2	0.211	0.	0.000	0.417	-0.001	0.848	0.	-0
3	-0.349	-0.	0.000	0.732	0.000	-0.144	0.	0
4	-0.334	0.	0.000	0.400	0.001	-0.293	0.	-0
5	0.000	-0.	0.760	0.000	0.121	0.000	0.	0
6	0.000	-0.	-0.517	0.000	0.574	0.001	-0.	0
7	0.000	0.	0.394	0.000	0.531	0.000	-0.	0
8	0.000	0.	-0.007	0.000	0.612	0.001	0.	0

Table S16: Effective Hamiltonian for NCS symmetric structure (2.33 Å)

CSFs	1	2	3	4	5	6	7	8
1	0.00	4.24	-3.43	4.60	0.00	0.00	0.	0
2	4.24	10.68	-0.19	-5.27	0.00	0.00	0.	0
3	-3.43	-0.19	11.50	1.60	0.00	0.00	0.	0
4	4.60	-5.27	1.60	13.64	0.00	0.00	0.	0
5	0.00	0.00	0.00	0.00	5.05	-4.29	1.	4
6	0.00	0.00	0.00	0.00	-4.29	5.87	4.	2
7	0.00	0.00	0.00	0.00	1.42	4.66	11.	-4
8	0.00	0.00	0.00	0.00	4.24	2.91	-4.	12

Eigenvalues after diagonalization: -4.45; -2.87; 8.66; 9.78; 12.38; 12.55; 17.23; 17.95

Table S17: GASSCF states and CI coefficients from the selected CSFs for NCS unsymmetric structure (2.28-2.38 Å). States 3, 4, 5, 8 and 11 are not a local doublet in the sigma manifold.

State	1	2	6	7	9	10	12	13
E (eV)	0.0	1.	12.9	14.0	17.0	17.1	21.	22
1	-0.850	0.	0.020	-0.343	-0.080	0.370	0.	-0
2	0.201	0.	-0.119	0.408	-0.084	0.854	-0.	0
3	-0.327	-0.	-0.053	0.729	-0.032	-0.163	0.	-0
4	0.326	-0.	0.044	-0.397	-0.138	0.257	0.	-0
5	0.040	-0.	-0.755	-0.136	0.091	0.028	-0.	0
6	-0.045	0.	-0.504	0.011	-0.567	-0.186	-0.	-0
7	0.040	-0.	0.395	0.035	-0.539	0.005	-0.	0
8	-0.040	0.	-0.015	0.020	0.588	0.043	-0.	-0

Table S18: Effective Hamiltonian for NCS unsymmetric structure (2.28-2.38 Å).

CSFs	1	2	3	4	5	6	7	8
1	0.00	-3.93	3.37	4.61	0.47	-0.57	0.	-0
2	-3.93	10.52	0.00	5.12	-1.40	1.35	-1.	1
3	3.37	0.00	11.65	-1.29	0.64	-1.13	0.	-0
4	4.61	5.12	-1.29	14.14	-0.51	0.54	-0.	0
5	0.47	-1.40	0.64	-0.51	5.27	4.07	-1.	4
6	-0.57	1.35	-1.13	0.54	4.07	6.32	4.	-2
7	0.55	-1.04	0.62	-0.79	-1.15	4.47	12.	4
8	-0.51	1.11	-0.64	0.90	4.00	-2.85	4.	13

Eigenvalues after diagonalization: -4.17; -2.54; 8.68; 9.85; 12.82; 12.95; 17.68; 18.42