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Supplementary Material

EXAFS and EPR Studies of the Alkene Oxidation Catalyst Species, *trans*-[Cr^{III}(bpb)$(L)_2$]$^{n+}$ and Cr(V) Oxidation Products (bpb = *N*,*N*´-Bis(2-pyridinecarboxamido)-1,2-benzene)

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Table S1. Characteristic IR bands of **1** and **2**

Wavenumber (cm^{-1})			
1.DMF.0.5H_2O	**1**.H_2O	**2**	Assignment
	3400-2700	3400-2400	νO–H
3061			νC–H
2941			νC–H
1626	1615	1610	amide I
1596	1591	1585	aromatic ring
1574	1561	1544	skeletal vibrations
1474	1473	1469	and C–H
1450	1449	1450	deformations
		1116	νCl–O
811	807	803	coordinated H_2O rock
755	754	754	C–H deformation

The sharp band due to the N–H stretch (at 3320 cm^{-1} for bpbH_2) was absent from the IR spectra of **1** and **2**, which showed that bpb was coordinated *via* the deprotonated amide N to the Cr. There was little difference in the position of most of the IR bands of **1** and **2**, though the position of the amide I band varied somewhat. This was probably because the amide group of the DMF of crystallization, which was in the sample of **1** produced by Method 1, also occurs in this region. The presence of the perchlorate counterion in **2** was confirmed by the νCl–O band at 1116 cm^{-1}. The band at ~810 cm^{-1} in the IR spectra was evidence that H_2O was coordinated in both products. The νCr–Cl vibration in Cr(III) complexes has been reported in the range 303-375 cm^{-1},[39-41] and the band at ~320 cm^{-1} (which was absent from the IR spectrum of $[Cr^{III}(bpb)(OH_2)_2]ClO_4$) may be due to νCr–Cl. However, as νCr–N vibrations also occur in the 300-400 cm^{-1} region,[39-41] the ligand in the second axial coordination site could not be unambiguously assigned from the low frequency region of the IR spectra, without isotopic substitution.

Table S2. Observed and calculated molecular isotope distributions for positive-ion ES/MS data for **2**

Molecular Formula	*m*/*z*	Relative Intensity Calculated	Relative Intensity Observed
$C_{18}H_{12}N_4O_2Cr$	366	5.2	5
	367	1.1	2
	368	100	100
	369	32.5	32
	370	7.7	10
	371	1.1	1
$C_{37}H_{27}N_8O_5Cr_2$	765	10.1	14
	766	5.5	6
	767	100	100
	768	65.4	68
	769	26.6	29
	770	7.5	11

Calculation of Determinancy

Parts of the bpb ligand were constrained to be planar and the bond lengths and angles within the bpb ligand were restrained using data on the ligand structure from crystal structures of it bound to other metal ions.[10,34-36] According to Binsted *et al*.,[37] additional independent observations are generated by the inclusion of distance information. The number of additional independent observations is equal to:

$$D(N-2)+1$$

Where *D* is the number of dimensions in which the refinement takes place (3 for the refinements in this paper), *N* is the number of atoms in the restrained unit of the molecule. For example, to include the effect of the bond length and angle restraints on the determinancy for Model **III**, the calculations are:

$$N_{idp} = \frac{2 \times 11.5 \times 4.0}{\pi} + [3(13-2)+1]$$

$$N_{idp} = 63$$

Parameters = 2+14+42

= 58

$$Determinancy = \frac{N_{idp}}{Parameters}$$

$$= 1.09$$

The C bonded to the axial O atom was not included in the refinement because, unlike the atoms in the bpb ligand, the bond length and angle data available do not allow tight restraints.

Table S3. Restraints used in MS fits of model **Ia** to the EXAFS data of **2**[a]

Restraints	
$S_0^2 \approx 0.9$ {0.2}	$\sigma^2_1 > 0.001$ {0.0005} Å^2
$\sigma^2_2 > 0.001$ {0.0005} Å^2	$\sigma^2_3 > 0.001$ {0.0005} Å^2
$\sigma^2_4 > 0.001$ {0.0005} Å^2	$\sigma^2_5 > 0.001$ {0.0005} Å^2
$\sigma^2_6 > 0.001$ {0.0005} Å^2	$\sigma^2_7 > 0.001$ {0.0005} Å^2
$\sigma^2_8 > 0.001$ {0.0005} Å^2	$\sigma^2_9 > 0.001$ {0.0005} Å^2
$\sigma^2_{10} > 0.001$ {0.0005} Å^2	$\sigma^2_{11} > 0.001$ {0.0005} Å^2
$\sigma^2_{12} > 0.001$ {0.0005} Å^2	$\sigma^2_{13} > 0.001$ {0.0005} Å^2
$\sigma^2_{14} > 0.001$ {0.0005} Å^2	$\sigma^2_{15} > 0.001$ {0.0005} Å^2
$\sigma^2_{16} > 0.001$ {0.0005} Å^2	$\sigma^2_{17} > 0.001$ {0.0005} Å^2
$\sigma^2_{18} > 0.001$ {0.0005} Å^2	$\sigma^2_{19} > 0.001$ {0.0005} Å^2
$\sigma^2_{20} > 0.001$ {0.0005} Å^2	$\sigma^2_{21} > 0.001$ {0.0005} Å^2
$\sigma^2_{22} > 0.001$ {0.0005} Å^2	$\sigma^2_{23} > 0.001$ {0.0005} Å^2
$\sigma^2_{24} > 0.001$ {0.0005} Å^2	$\sigma^2_{25} > 0.001$ {0.0005} Å^2
$\sigma^2_{26} > 0.001$ {0.0005} Å^2	$\sigma^2_1 < 0.02$ {0.01} Å^2
$\sigma^2_2 < 0.02$ {0.01} Å^2	$\sigma^2_3 < 0.02$ {0.01} Å^2
$\sigma^2_4 < 0.02$ {0.01} Å^2	$\sigma^2_5 < 0.02$ {0.01} Å^2
$\sigma^2_6 < 0.02$ {0.01} Å^2	$\sigma^2_7 < 0.02$ {0.01} Å^2
$\sigma^2_8 < 0.02$ {0.01} Å^2	$\sigma^2_9 < 0.02$ {0.01} Å^2
$\sigma^2_{10} < 0.02$ {0.01} Å^2	$\sigma^2_{11} < 0.02$ {0.01} Å^2
$\sigma^2_{12} < 0.02$ {0.01} Å^2	$\sigma^2_{13} < 0.03$ {0.01} Å^2
$\sigma^2_{14} < 0.03$ {0.01} Å^2	$\sigma^2_{15} < 0.03$ {0.01} Å^2
$\sigma^2_{16} < 0.03$ {0.01} Å^2	$\sigma^2_{17} < 0.02$ {0.01} Å^2
$\sigma^2_{18} < 0.03$ {0.01} Å^2	$\sigma^2_{19} < 0.03$ {0.01} Å^2
$\sigma^2_{20} < 0.03$ {0.01} Å^2	$\sigma^2_{21} < 0.02$ {0.01} Å^2
$\sigma^2_{22} < 0.02$ {0.01} Å^2	$\sigma^2_{23} < 0.03$ {0.01} Å^2
$\sigma^2_{24} < 0.03$ {0.01} Å^2	$\sigma^2_{25} < 0.03$ {0.01} Å^2
$\sigma^2_{26} < 0.02$ {0.01} Å^2	$\sigma^2_7 > (\sigma^2_2 + 0.001)$ {0.0005} Å^2
$\sigma^2_{13} > (\sigma^2_7 + 0.001)$ {0.0005} Å^2	$\sigma^2_{14} > (\sigma^2_{13} + 0.001)$ {0.0005} Å^2
$\sigma^2_{17} > (\sigma^2_1 + 0.001)$ {0.0005} Å^2	$\sigma^2_{18} > (\sigma^2_1 + 0.001)$ {0.0005} Å^2
$\sigma^2_{20} > (\sigma^2_1 + 0.001)$ {0.0005} Å^2	$\sigma^2_{21} > (\sigma^2_1 + 0.001)$ {0.0005} Å^2
$\sigma^2_{19} > (\sigma^2_{18} + 0.001)$ {0.0005} Å^2	$\sigma^2_{11} > (\sigma^2_9 + 0.001)$ {0.0005} Å^2
N1–C17 ≈ 1.35 {0.05} Å	N1–C21 ≈ 1.34 {0.05} Å
C17–C18 ≈ 1.38 {0.05} Å	C18–C19 ≈ 1.38 {0.05} Å
C19–C20 ≈ 1.36 {0.05} Å	C20–C21 ≈ 1.37 {0.05} Å
N2–C7 ≈ 1.41 {0.05} Å	N2–C9 ≈ 1.34 {0.05} Å
C9–O11 ≈ 1.23 {0.05} Å	C9–C17 ≈ 1.50 {0.05} Å
C7–C8 ≈ 1.42 {0.05} Å	C7–C13 ≈ 1.39 {0.05} Å
C13–C14 ≈ 1.38 {0.05} Å	C14–C15 ≈ 1.38 {0.05} Å
Cr0–O5 < 3.0 {0.1} Å	Cr0–O6 < 3.0 {0.1} Å
N1–Cr0–N2 ≈ 81 {10}°	N1–Cr0–N4 ≈ 108 {10}°
N2–Cr0–N3 ≈ 82 {10}°	Cr0–N1–C17 ≈ 112 {5}°

Cr0–N1–C21 ≈ 129 {5}°	C17–N1–C21 ≈ 118 {5}°
Cr0–N2–C7 ≈ 114 {5}°	Cr0–N2–C9 ≈ 119 {5}°
C7–N2–C9 ≈ 126 {5}°	N2–C9–O11 ≈ 129 {5}°
N2–C9–C17 ≈ 110 {5}°	O11–C9–C17 ≈ 120 {5}°
N2–C7–C8 ≈ 115 {5}°	N2–C7–C13 ≈ 126 {5}°
C8–C7–C13 ≈ 120 {5}°	N1–C17–C9 ≈ 117 {5}°
N1–C17–C18 ≈ 121 {5}°	C9–C17–C18 ≈ 121 {5}°
N1–C21–C20 ≈ 122 {5}°	C17–C18–C19 ≈ 119 {5}°
C18–C19–C20 ≈ 119 {5}°	C19–C20–C21 ≈ 119 {5}°
C7–C13–C14 ≈ 120 {5}°	C13–C14–C13 ≈ 120 {5}°
O5–Cr0–N1 > 80 {1}°	O5–Cr0–N2 > 80 {1}°
O5–Cr0–N3 > 80 {1}°	O5–Cr0–N4 > 80 {1}°
O6–Cr0–N1 > 80 {1}°	O6–Cr0–N2 > 80 {1}°
O6–Cr0–N3 > 80 {1}°	O6–Cr0–N4 > 80 {1}°
Atoms restrained to be approximately coplanar:[b]	
((C7–C13)×(C8–C13))^.(C14–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C15–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C16–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(N2–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(N3–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C9–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C10–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(O11–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(O12–C13) ≈ 0 {0.01}°	
((N1–C17)×(C18–C17))^.(C19–C17) ≈ 0 {0.01}°	
((N1–C17)×(C18–C17))^.(C20–C17) ≈ 0 {0.01}°	
((N1–C17)×(C18–C17))^.(C21–C17) ≈ 0 {0.01}°	

[a] The ranges of the restraints are given in parentheses. [b] The vector dot product of the vector from atom4-atom2 with the vector cross product of the vectors atom1-atom2 and atom3-atom2 is restrained to be zero.

Table S4. Constraints used in MS fit of model **Ia** to the EXAFS data of **2**

Constraints	
$\sigma^2{}_1 = \sigma^2{}_4$	$\sigma^2{}_2 = \sigma^2{}_3$
$\sigma^2{}_7 = \sigma^2{}_8$	$\sigma^2{}_9 = \sigma^2{}_{10}$
$\sigma^2{}_{11} = \sigma^2{}_{12}$	$\sigma^2{}_{13} = \sigma^2{}_{16}$
$\sigma^2{}_{14} = \sigma^2{}_{15}$	$\sigma^2{}_{17} = \sigma^2{}_{22}$
$\sigma^2{}_{18} = \sigma^2{}_{23}$	$\sigma^2{}_{19} = \sigma^2{}_{24}$
$\sigma^2{}_{20} = \sigma^2{}_{25}$	$\sigma^2{}_{21} = \sigma^2{}_{26}$
$x1 = x4$	$y1 = –y4$
$z1 = z4$	$x2 = x3$
$y2 = –y3$	$z2 = z3$
$x7 = x8$	$y7 = –y8$
$z7 = z8$	$x9 = x10$
$y9 = –y10$	$z9 = z10$
$x11 = x12$	$y11 = –y12$
$z11 = z12$	$x13 = x16$
$y13 = –y16$	$z13 = z16$
$x14 = x15$	$y14 = –y15$
$z14 = z15$	$x17 = x22$
$y17 = –y22$	$z17 = z22$
$x18 = x23$	$y18 = –y23$
$z18 = z23$	$x19 = x24$
$y19 = –y24$	$z19 = z24$
$x20 = x25$	$y20 = –y25$
$z20 = z25$	$x21 = x26$
$y21 = –y26$	$z21 = z26$

Table S5. Details of the SS and MS paths obtained from the MS fit of model **Ia** to the EXAFS data of **2**

Path No.	Atoms in MS pathway[a]	Degeneracy	R^b (Å)	Importance factor[c]
1	Cr0→N2→Cr0	2	1.94	100
2	Cr0→O5→Cr0	1	1.95	49.9
3	Cr0→O6→Cr0	1	2.03	51.4
4	Cr0→N1→Cr0	2	2.07	96.2
5	Cr0→C7→Cr0	2	2.82	26.0
6	Cr0→C10→Cr0	2	2.87	44.6
7	Cr0→C22→Cr0	2	2.87	42.3
8	Cr0→C7→N2→Cr0	4	3.08	16.2
9	Cr0→C9→N2→Cr0	4	3.08	31.8
10	Cr0→C26→Cr0	2	3.10	32.8
11	Cr0→C17→N1→Cr0	4	3.15	23.0
12	Cr0→O5→N3→Cr0	2	3.19	5.11
13	Cr0→N2→N3→Cr0	2	3.23	4.77
14	Cr0→O6→N3→Cr0	2	3.26	10.5
15	Cr0→C26→N4→Cr0	4	3.26	38.5
16	Cr0→N4→N3→Cr0	4	3.28	10.1
17	Cr0→N2→C9→N2→Cr0	2	3.29	7.81
18	Cr0→O5→N2→Cr0	2	3.30	4.34
19	Cr0→N2→C7→N2→Cr0	2	3.35	2.73
20	Cr0→N4→O6→Cr0	4	3.37	10.0
21	Cr0→N4→C26→N4→Cr0	2	3.42	13.8
22	Cr0→N1→C17→N1→Cr0	2	3.42	3.63
23	Cr0→C7→C8→Cr0	2	3.52	3.97
24	Cr0→C7→N3→Cr0	4	3.57	6.76
25	Cr0→C22→N3→Cr0	4	3.57	9.32
26	Cr0→N4→O5→Cr0	2	3.61	3.63
27	Cr0→C17→C9→Cr0	4	3.62	11.5
28	Cr0→C10→N4→Cr0	4	3.68	8.25
29	Cr0→N1→O5→Cr0	2	3.71	6.03
30	Cr0→N4→N1→Cr0	2	3.78	4.90
31	Cr0→N3→Cr0→N3→Cr0	2	3.88	7.38
32	Cr0→O5→Cr0→O5→Cr0	1	3.89	3.47
33	Cr0→O5→O6→Cr0	2	3.94	13.4
34	Cr0→N2→N4→Cr0	4	3.96	27.0
35	Cr0→O6→Cr0→N2→Cr0	4	3.97	4.28
36	Cr0→O5→Cr0→O6→Cr0	2	3.98	16.9
37	Cr0→C8→O6→Cr0	4	4.00	3.72
38	Cr0→N3→Cr0→N1→Cr0	4	4.01	32.1
39	Cr0→N4→Cr0→N3→Cr0	4	4.01	4.49
40	Cr0→O6→Cr0→O6→Cr0	1	4.06	3.35

41	Cr0→C9→C7→Cr0	4	4.07	3.75
42	Cr0→O11→Cr0	2	4.07	20.2
43	Cr0→O12→C10→Cr0	4	4.09	43.1
44	Cr0→N1→Cr0→O6→Cr0	4	4.10	3.48
45	Cr0→C10→O12→C10→Cr0	2	4.10	25.9
46	Cr0→C10→O6→Cr0	4	4.12	4.38
47	Cr0→C21→C17→Cr0	4	4.14	4.84
48	Cr0→N4→Cr0→N4→Cr0	2	4.14	5.58
49	Cr0→C16→Cr0	2	4.17	10.7
50	Cr0→O11→N2→Cr0	4	4.17	26.6
51	Cr0→C9→O5→Cr0	4	4.18	3.20
52	Cr0→C13→C7→Cr0	4	4.18	21.0
53	Cr0→C9→O11→N2→Cr0	4	4.19	27.4
54	Cr0→C7→C13→C7→Cr0	2	4.20	12.7
55	Cr0→C18→Cr0	2	4.20	17.4
56	Cr0→C7→N2→C7→Cr0	2	4.22	1.88
57	Cr0→C9→N2→C7→Cr0	4	4.22	5.95
58	Cr0→C9→N2→C9→Cr0	2	4.22	8.00
59	Cr0→C17→N1→C17→Cr0	2	4.22	6.36
60	Cr0→C32→C22→Cr0	4	4.23	33.8
61	Cr0→C17→C18→C17→Cr0	2	4.25	19.1
62	Cr0→N3→O12→N3→Cr0	2	4.27	10.1
63	Cr0→N2→C9→C7→Cr0	4	4.28	4.24
64	Cr0→C13→N2→Cr0	4	4.30	13.0
65	Cr0→O11→C9→N2→Cr0	4	4.30	15.7
66	Cr0→N4→C26→C22→Cr0	4	4.30	5.18
67	Cr0→C7→C13→N2→Cr0	4	4.31	13.5
68	Cr0→C18→N1→Cr0	4	4.33	20.6
69	Cr0→N3→C8→C10→Cr0	4	4.33	3.12
70	Cr0→C17→O5→Cr0	4	4.34	3.30
71	Cr0→C26→N4→C22→Cr0	4	4.34	6.90
72	Cr0→C17→N1→N2→Cr0	4	4.35	3.15
73	Cr0→C17→C18→N1→Cr0	4	4.35	19.7
74	Cr0→C9→N3→Cr0	4	4.36	4.76
75	Cr0→C8→N3→N2→Cr0	4	4.37	2.19
76	Cr0→C10→N3→N2→Cr0	4	4.37	5.69
77	Cr0→C25→Cr0	2	4.37	7.43
78	Cr0→C7→N1→Cr0	4	4.40	2.71
79	Cr0→C25→N4→Cr0	4	4.41	14.1
80	Cr0→C8→N3→N4→Cr0	4	4.42	3.03
81	Cr0→C25→C26→Cr0	4	4.42	14.3
82	Cr0→C9→N2→N1→Cr0	4	4.42	2.81
83	Cr0→N1→C17→C21→Cr0	4	4.42	4.29

84	Cr0→N3→C16→N3→Cr0	2	4.43	4.67
85	Cr0→N3→O5→N3→Cr0	2	4.44	3.43
86	Cr0→C13→C7→N2→Cr0	4	4.45	6.84
87	Cr0→C26→N3→Cr0	4	4.45	2.60
88	Cr0→C26→N4→C26→Cr0	2	4.45	6.84
89	Cr0→N1→C20→N1→Cr0	2	4.45	5.89
90	Cr0→N4→C23→N4→Cr0	2	4.45	7.19
91	Cr0→C26→C25→N4→Cr0	4	4.46	10.8
92	Cr0→C26→N4→N3→Cr0	4	4.47	3.02
93	Cr0→C26→C25→C26→Cr0	2	4.47	6.08
94	Cr0→N3→O6→N3→Cr0	2	4.49	3.11
95	Cr0→N3→N4→N3→Cr0	2	4.49	3.02
96	Cr0→C18→C17→N1→Cr0	4	4.50	10.0
97	Cr0→N3→N2→N3→Cr0	2	4.53	3.43
98	Cr0→O6→N2→O6→Cr0	2	4.58	3.13
99	Cr0→C20→C21→N1→Cr0	4	4.58	6.57
100	Cr0→N1→N2→N1→Cr0	2	4.62	3.08
101	Cr0→C22→N2→Cr0	4	4.64	10.5
102	Cr0→O11→C17→Cr0	4	4.66	2.73
103	Cr0→O6→N1→O6→Cr0	2	4.67	2.86
104	Cr0→C10→O12→C22→Cr0	4	2.67	3.90
105	Cr0→C8→N1→Cr0	4	4.69	6.28
106	Cr0→C16→C7→Cr0	4	4.70	2.07
107	Cr0→C10→N3→C7→Cr0	4	4.70	1.96
108	Cr0→N4→O6→N4→Cr0	2	4.70	2.84
109	Cr0→C7→N2→C8→Cr0	4	4.71	3.08
110	Cr0→C22→N3→C8→Cr0	4	4.71	1.72
111	Cr0→C9→N2→C17→Cr0	4	4.71	6.10
112	Cr0→C7→C13→C8→Cr0	4	4.72	2.50
113	Cr0→C8→Cr0→N2→Cr0	4	4.76	2.73
114	Cr0→C22→N4→C10→Cr0	4	4.76	5.27
115	Cr0→C17→N4→Cr0	4	4.77	10.2
116	Cr0→C21→O5→Cr0	4	4.77	6.11
117	Cr0→C18→C9→Cr0	4	4.78	2.86
118	Cr0→C9→Cr0→N2→Cr0	4	4.81	2.77
119	Cr0→C24→Cr0	2	4.81	12.2
120	Cr0→C17→Cr0→N3→Cr0	4	4.81	7.01
121	Cr0→C17→C18→C9→Cr0	4	4.81	3.61
122	Cr0→C22→Cr0→N3→Cr0	4	4.81	3.56
123	Cr0→C19→N1→Cr0	4	4.82	20.8
124	Cr0→N1→C19→N1→Cr0	2	4.83	10.2
125	Cr0→O12→C10→C22→Cr0	4	4.84	5.34
126	Cr0→C8→N2→N3→Cr0	4	4.86	3.27

127	Cr0→C22→N3→N2→Cr0	4	4.86	3.81
128	Cr0→C9→O11→N1→Cr0	4	4.86	4.28
129	Cr0→C17→N1→N4→Cr0	4	4.86	6.91
130	Cr0→C18→N2→Cr0	4	4.87	3.08
131	Cr0→C26→N4→C10→Cr0	4	4.87	2.58
132	Cr0→N2→C9→C8	4	4.88	2.60
133	Cr0→C7→Cr0→N4→Cr0	4	4.89	3.92
134	Cr0→C13→C7→C8→Cr0	4	4.89	2.38
135	Cr0→C9→N1→N2→Cr0	4	4.89	4.18
136	Cr0→C17→C18→N2→Cr0	4	4.89	4.05
137	Cr0→C7→C13→N3→Cr0	4	4.90	2.78
138	Cr0→C8→N2→N1→Cr0	4	4.90	2.38
139	Cr0→O11→C9→N1→Cr0	4	4.90	4.69
140	Cr0→N4→C9→Cr0	4	4.91	15.1
141	Cr0→C21→N1→O5→Cr0	4	4.91	4.19
142	Cr0→C22→N3→N4→Cr0	4	4.91	4.43
143	Cr0→N3→C17→N1→Cr0	4	4.92	3.70
144	Cr0→N4→Cr0→C9→Cr0	4	4.94	16.8
145	Cr0→C9→Cr0→N1→Cr0	4	4.94	3.13
146	Cr0→C22→Cr0→N1→Cr0	4	3.94	6.87
147	Cr0→N2→C7→C17→Cr0	4	4.95	2.02
148	Cr0→N4→C7→N2→Cr0	4	4.95	2.60
149	Cr0→N4→C26→C10→Cr0	4	4.97	3.46
150	Cr0→C20→C17→Cr0	4	4.98	1.26
151	Cr0→N2→C26→Cr0	4	4.99	12.6
152	Cr0→N1→C20→C17→Cr0	4	5.02	1.41
153	Cr0→C24→C22→Cr0	4	5.03	8.84
154	Cr0→N3→Cr0→C21→Cr0	4	5.04	12.5
155	Cr0→C17→N1→N3→Cr0	4	5.04	2.48
156	Cr0→C17→C19→N1→Cr0	4	5.04	7.36
157	Cr0→N4→C22→N1→Cr0	4	5.05	3.18
158	Cr0→C26→Cr0→O5→Cr0	4	5.05	1.81
159	Cr0→C10→N3→N1→Cr0	4	5.10	7.55
160	Cr0→N2→C9→N4→Cr0	4	5.12	6.86
161	Cr0→C24→C26→Cr0	4	5.13	5.84
162	Cr0→N1→C19→C21→Cr0	4	5.14	5.36
163	Cr0→N4→C26→N2→Cr0	4	5.15	7.99
164	Cr0→C14→Cr0	2	5.16	4.82
165	Cr0→C21→N1→N3→Cr0	4	5.16	7.63
166	Cr0→N1→C21→C18→Cr0	4	5.16	4.18
167	Cr0→C22→C7→Cr0	4	5.17	1.91
168	Cr0→C26→Cr0→N4→Cr0	4	5.17	2.23
169	Cr0→C14→C7→Cr0	4	5.18	8.25

170	Cr0→C7→N3→C7→Cr0	2	5.19	0.64
171	Cr0→N3→C8→O12→Cr0	4	5.19	2.14
172	Cr0→C17→N2→C8→Cr0	4	5.19	1.60
173	Cr0→C8→C15→C8→Cr0	2	5.20	3.12
174	Cr0→C24→C23→Cr0	4	5.20	4.01
175	Cr0→C22→N3→C22→Cr0	2	5.20	2.09
176	Cr0→C18→C19→N1→Cr0	4	5.20	3.53
177	Cr0→C19→C18→C17→Cr0	4	5.22	5.05
178	Cr0→N2→C9→C13→Cr0	4	5.23	2.77
179	Cr0→C7→O6→N2→Cr0	4	5.23	2.24
180	Cr0→C25→C22→N4→Cr0	4	5.26	1.83
181	Cr0→C19→C20→Cr0	4	5.27	2.78
182	Cr0→C25→C24→N4→Cr0	4	5.28	2.35
183	Cr0→O11→C9→O11→Cr0	2	5.31	5.78
184	Cr0→O11→N2→C9→Cr0	4	5.31	6.62
185	Cr0→C24→C25→C26→Cr0	4	5.32	2.88
186	Cr0→C9→O6→N2→Cr0	4	5.35	3.16
187	Cr0→C15→C16→Cr0	4	5.35	4.30
188	Cr0→O5→N1→O5→Cr0	2	5.36	2.57
189	Cr0→C15→C16→C8→Cr0	4	5.37	4.17
190	Cr0→C14→C8→Cr0	4	5.37	3.74
191	Cr0→C13→C14→C7→Cr0	4	5.37	4.04
192	Cr0→C8→C14→C7→Cr0	4	5.39	3.13
193	Cr0→C18→N1→C17→Cr0	4	5.40	5.33
194	Cr0→C15→N3→Cr0	4	5.41	3.59
195	Cr0→N2→O6→C26→Cr0	4	5.43	2.43
196	Cr0→C7→C14→N2→Cr0	4	5.43	3.55
197	Cr0→C13→N2→C7→Cr0	4	5.44	2.66
198	Cr0→C15→C8→N3→Cr0	4	5.45	3.35
199	Cr0→C17→O6→N1→Cr0	4	5.45	2.98
200	Cr0→C15→C16→N3→Cr0	4	5.48	3.63
201	Cr0→C10→C9→Cr0	2	5.48	2.59
202	Cr0→C10→N2→C9→Cr0	4	5.50	5.27
203	Cr0→C9→O5→N2→Cr0	4	5.53	3.40

[a] The atom numbering scheme is shown in Figure 1. [b] *R* is the total distance travelled by the photoelectron divided by two. [c] The importance factor is the percent contribution of a path relative to the strongest MS path and includes Debye-Waller contributions.

Table S6. Debye-Waller factors for model **Ia** of **2**[a]

atom	σ^2 (Å^2)	atom	σ^2 (Å^2)
N1	0.0010(1)	N2	0.0011(1)
O5	0.0026(4)	O6	0.0010(1)
C7	0.021(1)	C9	0.0010(1)
O11	0.0024(2)	C13	0.022(1)
C14	0.030(1)	C17	0.0026(3)
C18	0.0020(1)	C19	0.0030(6)
C20	0.031(1)	C21	0.0037(4)

[a] The Monte-Carlo errors in the last significant figure are given in parentheses.

Table S7. Restraints used in MS fits of model **III** to the EXAFS data of **1**·DMF·0.5H_2O[a]

Restraints	
$S_0^2 \approx 0.9$ {0.2}	$\sigma^2_{1} > 0.001$ {0.0005} Å^2
$\sigma^2_{2} > 0.001$ {0.0005} Å^2	$\sigma^2_{3} > 0.001$ {0.0005} Å^2
$\sigma^2_{4} > 0.001$ {0.0005} Å^2	$\sigma^2_{5} > 0.001$ {0.0005} Å^2
$\sigma^2_{6} > 0.001$ {0.0005} Å^2	$\sigma^2_{7} > 0.001$ {0.0005} Å^2
$\sigma^2_{8} > 0.001$ {0.0005} Å^2	$\sigma^2_{9} > 0.001$ {0.0005} Å^2
$\sigma^2_{10} > 0.001$ {0.0005} Å^2	$\sigma^2_{11} > 0.001$ {0.0005} Å^2
$\sigma^2_{12} > 0.001$ {0.0005} Å^2	$\sigma^2_{13} > 0.001$ {0.0005} Å^2
$\sigma^2_{14} > 0.001$ {0.0005} Å^2	$\sigma^2_{15} > 0.001$ {0.0005} Å^2
$\sigma^2_{16} > 0.001$ {0.0005} Å^2	$\sigma^2_{17} > 0.001$ {0.0005} Å^2
$\sigma^2_{18} > 0.001$ {0.0005} Å^2	$\sigma^2_{19} > 0.001$ {0.0005} Å^2
$\sigma^2_{20} > 0.001$ {0.0005} Å^2	$\sigma^2_{21} > 0.001$ {0.0005} Å^2
$\sigma^2_{22} > 0.001$ {0.0005} Å^2	$\sigma^2_{23} > 0.001$ {0.0005} Å^2
$\sigma^2_{24} > 0.001$ {0.0005} Å^2	$\sigma^2_{25} > 0.001$ {0.0005} Å^2
$\sigma^2_{26} > 0.001$ {0.0005} Å^2	$\sigma^2_{1} < 0.02$ {0.01} Å^2
$\sigma^2_{2} < 0.02$ {0.01} Å^2	$\sigma^2_{3} < 0.02$ {0.01} Å^2
$\sigma^2_{4} < 0.02$ {0.01} Å^2	$\sigma^2_{5} < 0.02$ {0.01} Å^2
$\sigma^2_{6} < 0.02$ {0.01} Å^2	$\sigma^2_{7} < 0.02$ {0.01} Å^2
$\sigma^2_{8} < 0.02$ {0.01} Å^2	$\sigma^2_{9} < 0.02$ {0.01} Å^2
$\sigma^2_{10} < 0.02$ {0.01} Å^2	$\sigma^2_{11} < 0.02$ {0.01} Å^2
$\sigma^2_{12} < 0.02$ {0.01} Å^2	$\sigma^2_{13} < 0.03$ {0.01} Å^2
$\sigma^2_{14} < 0.03$ {0.01} Å^2	$\sigma^2_{15} < 0.03$ {0.01} Å^2
$\sigma^2_{16} < 0.03$ {0.01} Å^2	$\sigma^2_{17} < 0.02$ {0.01} Å^2
$\sigma^2_{18} < 0.03$ {0.01} Å^2	$\sigma^2_{19} < 0.03$ {0.01} Å^2
$\sigma^2_{20} < 0.03$ {0.01} Å^2	$\sigma^2_{21} < 0.02$ {0.01} Å^2
$\sigma^2_{22} < 0.02$ {0.01} Å^2	$\sigma^2_{23} < 0.03$ {0.01} Å^2
$\sigma^2_{24} < 0.03$ {0.01} Å^2	$\sigma^2_{25} < 0.03$ {0.01} Å^2
$\sigma^2_{26} < 0.02$ {0.01} Å^2	$\sigma^2_{7} > (\sigma^2_{2} + 0.001)$ {0.0005} Å^2
$\sigma^2_{13} > (\sigma^2_{7} + 0.001)$ {0.0005} Å^2	$\sigma^2_{14} > (\sigma^2_{13} + 0.001)$ {0.0005} Å^2
$\sigma^2_{17} > (\sigma^2_{1} + 0.001)$ {0.0005} Å^2	$\sigma^2_{18} > (\sigma^2_{1} + 0.001)$ {0.0005} Å^2
$\sigma^2_{20} > (\sigma^2_{1} + 0.001)$ {0.0005} Å^2	$\sigma^2_{21} > (\sigma^2_{1} + 0.001)$ {0.0005} Å^2
$\sigma^2_{19} > (\sigma^2_{18} + 0.001)$ {0.0005} Å^2	$\sigma^2_{11} > (\sigma^2_{9} + 0.001)$ {0.0005} Å^2
N1–C17 ≈ 1.35 {0.05} Å	N1–C21 ≈ 1.34 {0.05} Å
C17–C18 ≈ 1.38 {0.05} Å	C18–C19 ≈ 1.38 {0.05} Å
C19–C20 ≈ 1.36 {0.05} Å	C20–C21 ≈ 1.37 {0.05} Å
N2–C7 ≈ 1.41 {0.05} Å	N2–C9 ≈ 1.34 {0.05} Å
C9–O11 ≈ 1.23 {0.05} Å	C9–C17 ≈ 1.50 {0.05} Å
C7–C8 ≈ 1.42 {0.05} Å	C7–C13 ≈ 1.39 {0.05} Å
C13–C14 ≈ 1.38 {0.05} Å	C14–C15 ≈ 1.38 {0.05} Å
Cr0–O5 < 3.0 {0.1} Å	Cr0–Cl6 < 3.5 {0.1} Å
N1–Cr0–N2 ≈ 81 {10}°	N1–Cr0–N4 ≈ 108 {10}°
N2–Cr0–N3 ≈ 82 {10}°	Cr0–N1–C17 ≈ 112 {5}°

Cr0–N1–C21 ≈ 129 {5}°	C17–N1–C21 ≈ 118 {5}°
Cr0–N2–C7 ≈ 114 {5}°	Cr0–N2–C9 ≈ 119 {5}°
C7–N2–C9 ≈ 126 {5}°	N2–C9–O11 ≈ 129 {5}°
N2–C9–C17 ≈ 110 {5}°	O11–C9–C17 ≈ 120 {5}°
N2–C7–C8 ≈ 115 {5}°	N2–C7–C13 ≈ 126 {5}°
C8–C7–C13 ≈ 120 {5}°	N1–C17–C9 ≈ 117 {5}°
N1–C17–C18 ≈ 121 {5}°	C9–C17–C18 ≈ 121 {5}°
N1–C21–C20 ≈ 122 {5}°	C17–C18–C19 ≈ 119 {5}°
C18–C19–C20 ≈ 119 {5}°	C19–C20–C21 ≈ 119 {5}°
C7–C13–C14 ≈ 120 {5}°	C13–C14–C13 ≈ 120 {5}°
O5–Cr0–N1 > 80 {1}°	O5–Cr0–N2 > 80 {1}°
O5–Cr0–N3 > 80 {1}°	O5–Cr0–N4 > 80 {1}°
Cl6–Cr0–N1 > 80 {1}°	Cl6–Cr0–N2 > 80 {1}°
Cl6–Cr0–N3 > 80 {1}°	Cl6–Cr0–N4 > 80 {1}°
Atoms restrained to be approximately coplanar:[b]	
((C7–C13)×(C8–C13))^.(C14–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C15–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C16–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(N2–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(N3–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C9–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(C10–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(O11–C13) ≈ 0 {0.01}°	
((C7–C13)×(C8–C13))^.(O12–C13) ≈ 0 {0.01}°	
((N1–C17)×(C18–C17))^.(C19–C17) ≈ 0 {0.01}°	
((N1–C17)×(C18–C17))^.(C20–C17) ≈ 0 {0.01}°	
((N1–C17)×(C18–C17))^.(C21–C17) ≈ 0 {0.01}°	

[a] The ranges of the restraints are given in parentheses. [b] The vector dot product of the vector from atom4-atom2 with the vector cross product of the vectors atom1-atom2 and atom3-atom2 is restrained to be zero.

Table S8. Constraints used in MS fits of model **III** to the EXAFS data of **1**·DMF·0.5H_2O

Constraints	
$\sigma^2_1 = \sigma^2_4$	$\sigma^2_2 = \sigma^2_3$
$\sigma^2_7 = \sigma^2_8$	$\sigma^2_9 = \sigma^2_{10}$
$\sigma^2_{11} = \sigma^2_{12}$	$\sigma^2_{13} = \sigma^2_{16}$
$\sigma^2_{14} = \sigma^2_{15}$	$\sigma^2_{17} = \sigma^2_{22}$
$\sigma^2_{18} = \sigma^2_{23}$	$\sigma^2_{19} = \sigma^2_{24}$
$\sigma^2_{20} = \sigma^2_{25}$	$\sigma^2_{21} = \sigma^2_{26}$
$x1 = x4$	$y1 = -y4$
$z1 = z4$	$x2 = x3$
$y2 = -y3$	$z2 = z3$
$x7 = x8$	$y7 = -y8$
$z7 = z8$	$x9 = x10$
$y9 = -y10$	$z9 = z10$
$x11 = x12$	$y11 = -y12$
$z11 = z12$	$x13 = x16$
$y13 = -y16$	$z13 = z16$
$x14 = x15$	$y14 = -y15$
$z14 = z15$	$x17 = x22$
$y17 = -y22$	$z17 = z22$
$x18 = x23$	$y18 = -y23$
$z18 = z23$	$x19 = x24$
$y19 = -y24$	$z19 = z24$
$x20 = x25$	$y20 = -y25$
$z20 = z25$	$x21 = x26$
$y21 = -y26$	$z21 = z26$

Table S9. Details of the SS and MS paths obtained from the MS fit of model **III** to the EXAFS data of **1**·DMF·0.5H_2O

Path No.	Atoms in MS pathway[a]	Degeneracy	R^b (Å)	Importance factor[c]
1	Cr0→O5→Cr0	1	1.91	100
2	Cr0→N3→Cr0	2	1.98	100
3	Cr0→N4→Cr0	2	2.07	98.0
4	Cr0→Cl6→Cr0	1	2.32	38.6
5	Cr0→C22→Cr0	2	2.86	28.6
6	Cr0→C7→Cr0	2	2.88	46.1
7	Cr0→C9→Cr0	2	2.88	46.9
8	Cr0→C26→Cr0	2	3.09	26.8
9	Cr0→C10→N3→Cr0	4	3.10	33.1
10	Cr0→C8→N3→Cr0	4	3.14	27.5
11	Cr0→C22→N4→Cr0	4	3.14	17.9
12	Cr0→N2→O5→Cr0	4	3.24	10.9
13	Cr0→C26→N4→Cr0	4	3.25	34.5
14	Cr0→N2→N3→Cr0	2	3.28	5.44
15	Cr0→N1→N2→Cr0	4	3.32	11.4
16	Cr0→N2→C9→N2→Cr0	2	3.32	8.10
17	Cr0→N3→C8→N3→Cr0	2	3.40	5.53
18	Cr0→N4→C26→N4→Cr0	2	3.41	13.1
19	Cr0→N4→C22→N4→Cr0	2	3.42	3.1
20	Cr0→Cl6→N3→Cr0	4	3.54	6.77
21	Cr0→N1→O5→Cr0	2	3.58	4.02
22	Cr0→C17→N2→Cr0	4	3.59	8.32
23	Cr0→C8→C7→Cr0	2	3.59	7.62
24	Cr0→Cl6→N4→Cr0	4	3.61	6.55
25	Cr0→C7→N3→Cr0	4	3.62	10.8
26	Cr0→C10→C22→Cr0	4	3.63	10.9
27	Cr0→N4→O5→Cr0	2	3.66	6.42
28	Cr0→C9→N1→Cr0	4	3.70	9.85
29	Cr0→N4→N1→Cr0	2	3.79	5.88
30	Cr0→O5→Cr0→O5→Cr0	1	3.83	4.16
31	Cr0→N3→Cr0→O5→Cr0	4	3.90	1.23
32	Cr0→N3→Cr0→N3→Cr0	2	3.97	7.70
33	Cr0→N3→N1→Cr0	4	4.00	28.8
34	Cr0→C7→O5→Cr0	4	4.01	5.67
35	Cr0→C9→O5→Cr0	4	4.04	5.45
36	Cr0→N3→Cr0→N1→Cr0	4	4.05	33.5
37	Cr0→N4→Cr0→N3→Cr0	4	4.05	4.95
38	Cr0→O11→Cr0	2	4.09	20.9
39	Cr0→O11→C9→Cr0	4	4.10	44.9
40	Cr0→C9→C7→Cr0	4	4.11	5.68

41	Cr0→C9→O11→C9→Cr0	2	4.11	30.2
42	Cr0→C26→C22→Cr0	4	4.14	3.39
43	Cr0→N1→Cr0→N1→Cr0	2	4.14	6.52
44	Cr0→C18→Cr0	2	4.19	19.3
45	Cr0→O5→Cl6→Cr0	2	4.20	8.67
46	Cr0→O12→N3→Cr0	4	4.20	26.6
47	Cr0→C9→O11→N2→Cr0	4	4.21	30.3
48	Cr0→C23→C22→Cr0	4	4.22	36.9
49	Cr0→C22→N4→C22→Cr0	2	4.22	2.35
50	Cr0→C9→N2→C9→Cr0	2	4.22	9.30
51	Cr0→C16→Cr0	2	4.23	18.4
52	Cr0→O5→Cr0→Cl6→Cr0	2	4.23	11.2
53	Cr0→C17→C18→C17→Cr0	2	4.24	22.3
54	Cr0→C13→C7→Cr0	4	4.25	36.7
55	Cr0→C9→N2→C7→Cr0	4	4.26	9.85
56	Cr0→C7→C13→C7→Cr0	2	4.26	23.2
57	Cr0→C7→N2→C7→Cr0	2	4.29	7.79
58	Cr0→N1→C21→C17→Cr0	4	4.30	3.83
59	Cr0→N2→O11→N2→Cr0	2	4.31	10.3
60	Cr0→C18→N1→Cr0	4	4.32	22.1
61	Cr0→O11→C9→N2→Cr0	4	4.32	18.1
62	Cr0→C26→N4→C22→Cr0	4	4.32	4.85
63	Cr0→N2→C9→C7→Cr0	4	4.33	6.28
64	Cr0→C17→C18→N1→Cr0	4	4.34	23.7
65	Cr0→C25→Cr0	2	4.35	9.19
66	Cr0→C13→N2→Cr0	4	4.35	22.1
67	Cr0→C7→C13→N2→Cr0	4	4.37	23.3
68	Cr0→N2→C7→C9→Cr0	4	4.37	5.17
69	Cr0→C10→N2→Cr0	4	4.39	4.56
70	Cr0→C17→N1→N2→Cr0	4	4.39	3.02
71	Cr0→C25→N4→Cr0	4	4.39	16.6
72	Cr0→C9→N2→N3→Cr0	4	4.40	5.95
73	Cr0→C25→C26→Cr0	4	4.40	16.3
74	Cr0→N1→C17→C21→Cr0	4	4.41	2.95
75	Cr0→C21→N1→C21→Cr0	2	4.43	3.33
76	Cr0→C8→N3→N2→Cr0	4	4.43	3.58
77	Cr0→C9→N2→N1→Cr0	4	4.44	3.48
78	Cr0→N4→C25→N4→Cr0	2	4.44	6.96
79	Cr0→N1→C18→N1→Cr0	2	4.44	8.23
80	Cr0→C26→C25→N4→Cr0	4	4.45	13.2
81	Cr0→C8→N4→Cr0	4	4.45	4.27
82	Cr0→C26→C25→C26→Cr0	2	4.46	7.30
83	Cr0→C7→N2→N1→Cr0	4	4.47	4.30

84	Cr0→N2→C13→N2→Cr0	2	4.48	8.07
85	Cr0→C21→N2→Cr0	4	4.48	2.14
86	Cr0→C21→N4→Cr0	4	4.48	1.94
87	Cr0→O5→N2→O5→Cr0	2	4.49	3.59
88	Cr0→C23→C22→N4→Cr0	4	4.49	11.8
89	Cr0→C26→N4→N3→Cr0	4	4.50	2.75
90	Cr0→C13→C7→N2→Cr0	4	4.51	12.9
91	Cr0→C20→C21→N1→Cr0	4	4.56	7.73
92	Cr0→N2→O5→N2→Cr0	2	4.57	3.85
93	Cr0→N3→N4→N3→Cr0	2	4.57	3.37
94	Cr0→N3→N2→N3→Cr0	2	4.58	3.69
95	Cr0→C21→O5→Cr0	4	4.63	3.76
96	Cr0→Cl6→Cr0→Cl6→Cr0	1	4.64	1.40
97	Cr0→N1→N2→N1→Cr0	2	4.65	3.40
98	Cr0→C22→N2→Cr0	4	4.66	7.73
99	Cr0→O12→C22→Cr0	4	4.66	2.95
100	Cr0→C9→O11→C17→Cr0	4	4.68	4.14
101	Cr0→C9→N2→C17→Cr0	4	4.71	5.51
102	Cr0→C8→N1→Cr0	4	4.74	9.98
103	Cr0→C22→N3→C8→Cr0	4	4.74	2.31
104	Cr0→C10→N3→C7→Cr0	4	4.74	3.49
105	Cr0→C16→C7→Cr0	4	4.76	4.03
106	Cr0→C21→N1→O5→Cr0	2	4.76	1.58
107	Cr0→C17→N1→C9→Cr0	4	4.77	4.73
108	Cr0→C17→N4→Cr0	4	4.77	7.90
109	Cr0→C8→N3→C7→Cr0	4	4.78	6.67
110	Cr0→C8→C16→C7→Cr0	4	4.78	4.97
111	Cr0→C23→C10→Cr0	4	4.79	3.54
112	Cr0→C19→Cr0	2	4.79	13.5
113	Cr0→N1→C21→O5→Cr0	4	4.79	2.31
114	Cr0→C24→N4→Cr0	4	4.80	23.1
115	Cr0→C22→C23→C10→Cr0	4	4.81	4.06
116	Cr0→N1→C19→N1→Cr0	2	4.81	12.4
117	Cr0→N4→Cl6→N2→Cr0	4	4.83	3.35
118	Cr0→C25→N4→O5→Cr0	2	4.84	1.78
119	Cr0→O12→C10→C22→Cr0	4	4.84	4.91
120	Cr0→C22→Cr0→N2→Cr0	4	4.85	4.62
121	Cr0→C22→Cr0→N3→Cr0	4	4.85	2.89
122	Cr0→C7→Cr0→N3→Cr0	4	4.86	4.13
123	Cr0→C10→Cr0→N3→Cr0	4	4.87	2.96
124	Cr0→C17→N1→N4→Cr0	4	4.87	6.01
125	Cr0→C10→O12→N4→Cr0	4	4.87	5.32
126	Cr0→C21→N1→C9→Cr0	4	4.88	2.45

127	Cr0→C17→N2→N3→Cr0	4	4.88	3.13
128	Cr0→C22→C23→N3→Cr0	4	4.90	4.91
129	Cr0→C7→N3→N3→Cr0	4	4.92	5.05
130	Cr0→O12→C10→N4→Cr0	4	4.92	5.70
131	Cr0→C17→N2→N1→Cr0	4	4.92	3.73
132	Cr0→N4→C9→Cr0	4	4.92	17.3
133	Cr0→N2→C9→C8→Cr0	4	4.93	3.98
134	Cr0→C22→Cr0→N1→Cr0	4	4.93	5.92
135	Cr0→N2→C22→N4→Cr0	4	4.94	3.26
136	Cr0→C10→N4→N3→Cr0	4	4.95	4.81
137	Cr0→C7→Cr0→N4→Cr0	4	4.95	5.87
138	Cr0→N1→Cr0→C10→Cr0	4	4.95	19.8
139	Cr0→C9→Cr0→N1→Cr0	4	4.95	3.74
140	Cr0→C13→C7→C8→Cr0	4	4.95	5.51
141	Cr0→C7→C13→N3→Cr0	4	4.96	4.83
142	Cr0→C8→N2→N1→Cr0	4	4.96	3.70
143	Cr0→C20→C17→Cr0	4	4.97	1.45
144	Cr0→N2→C7→C17→Cr0	4	4.98	2.53
145	Cr0→C18→C17→C9→Cr0	4	4.98	4.71
146	Cr0→N1→C21→C9→Cr0	4	4.98	3.12
147	Cr0→N1→C8→N3→Cr0	4	5.00	3.97
148	Cr0→C21→Cr0→O5→Cr0	4	5.00	1.60
149	Cr0→C24→C22→Cr0	4	5.01	8.95
150	Cr0→N1→C20→C17→Cr0	4	5.01	1.76
151	Cr0→N2→C26→Cr0	4	5.02	11.1
152	Cr0→C17→C19→N1→Cr0	4	5.02	8.52
153	Cr0→N1→C17→N4→Cr0	4	5.05	2.90
154	Cr0→N3→Cr0→C21→Cr0	4	5.07	11.3
155	Cr0→C22→N4→N2→Cr0	4	5.08	1.94
156	Cr0→C19→C21→Cr0	4	5.11	6.25
157	Cr0→C9→N2→N4→Cr0	4	5.12	8.50
158	Cr0→N4→C24→C26→Cr0	4	5.12	6.03
159	Cr0→N2→C9→N4→Cr0	4	5.14	7.48
160	Cr0→N1→C21→C18→Cr0	4	5.15	4.40
161	Cr0→C21→Cr0→N1→Cr0	4	5.16	1.96
162	Cr0→C19→C18→Cr0	4	5.18	4.46
163	Cr0→N4→C26→N2→Cr0	4	5.18	7.33
164	Cr0→C21→N1→N3→Cr0	4	5.18	7.19
165	Cr0→C22→N3→C22→Cr0	2	5.19	0.86
166	Cr0→C23→C24→N4→Cr0	4	5.19	4.51
167	Cr0→C8→C17→Cr0	4	5.20	2.07
168	Cr0→C24→C23→C22→Cr0	4	5.20	5.68
169	Cr0→N2→C7→O11→Cr0	4	5.22	3.53

170	Cr0→C15→Cr0	2	5.23	9.74
171	Cr0→C17→C19→C17→Cr0	2	5.24	1.96
172	Cr0→O5→N4→O5→Cr0	2	5.25	3.08
173	Cr0→C20→C17→N1→Cr0	4	5.25	2.01
174	Cr0→C19→C20→Cr0	4	5.25	3.20
175	Cr0→C15→C8→Cr0	4	5.25	17.0
176	Cr0→C8→N2→C8→Cr0	2	5.26	2.47
177	Cr0→C20→C19→N1→Cr0	4	5.26	3.12
178	Cr0→C7→C14→C7→Cr0	2	5.27	6.50
179	Cr0→N2→C9→C13→Cr0	4	5.29	4.51
180	Cr0→C24→C25→C26→Cr0	4	5.30	3.19
181	Cr0→O12→N3→C10→Cr0	4	5.32	7.62
182	Cr0→O12→C10→O12→Cr0	2	5.32	6.31
183	Cr0→C23→N4→C22→Cr0	4	5.39	4.92
184	Cr0→C14→C13→Cr0	4	5.42	8.84
185	Cr0→N4→N1→C9→Cr0	4	5.42	2.97
186	Cr0→C15→C16→Cr0	4	5.44	8.74
187	Cr0→C15→C7→Cr0	4	5.44	7.80
188	Cr0→C16→C15→C8→Cr0	4	5.44	8.49
189	Cr0→C8→O5→N3→Cr0	4	5.45	3.66
190	Cr0→C8→C14→C7→Cr0	4	5.46	6.44
191	Cr0→C15→N3→Cr0	4	5.47	7.14
192	Cr0→C9→C10→Cr0	2	5.49	2.77
193	Cr0→C7→C14→N2→Cr0	4	5.50	7.29

[a] The atom numbering scheme is shown in Figure 5.26. [b] *R* is the total distance travelled by the photoelectron divided by two. [c] The importance factor is the percent contribution of a path relative to the strongest MS path and includes Debye-Waller contributions.

Table S10. Debye-Waller factors for model **III** of **1**.DMF.0.5H_2O[a]

atom	σ^2 (Å^2)	atom	σ^2 (Å^2)
N1	0.0010(1)	N2	0.0010(1)
O5	0.0020(7)	Cl6	0.0038(3)
C7	0.0020(1)	C9	0.0010(1)
O11	0.003(1)	C13	0.0030(1)
C14	0.0040(1)	C17	0.020(1)
C18	0.0020(1)	C19	0.0030(6)
C20	0.030(1)	C21	0.018(1)

[a] The Monte-Carlo errors in the last significant figure are given in parentheses.

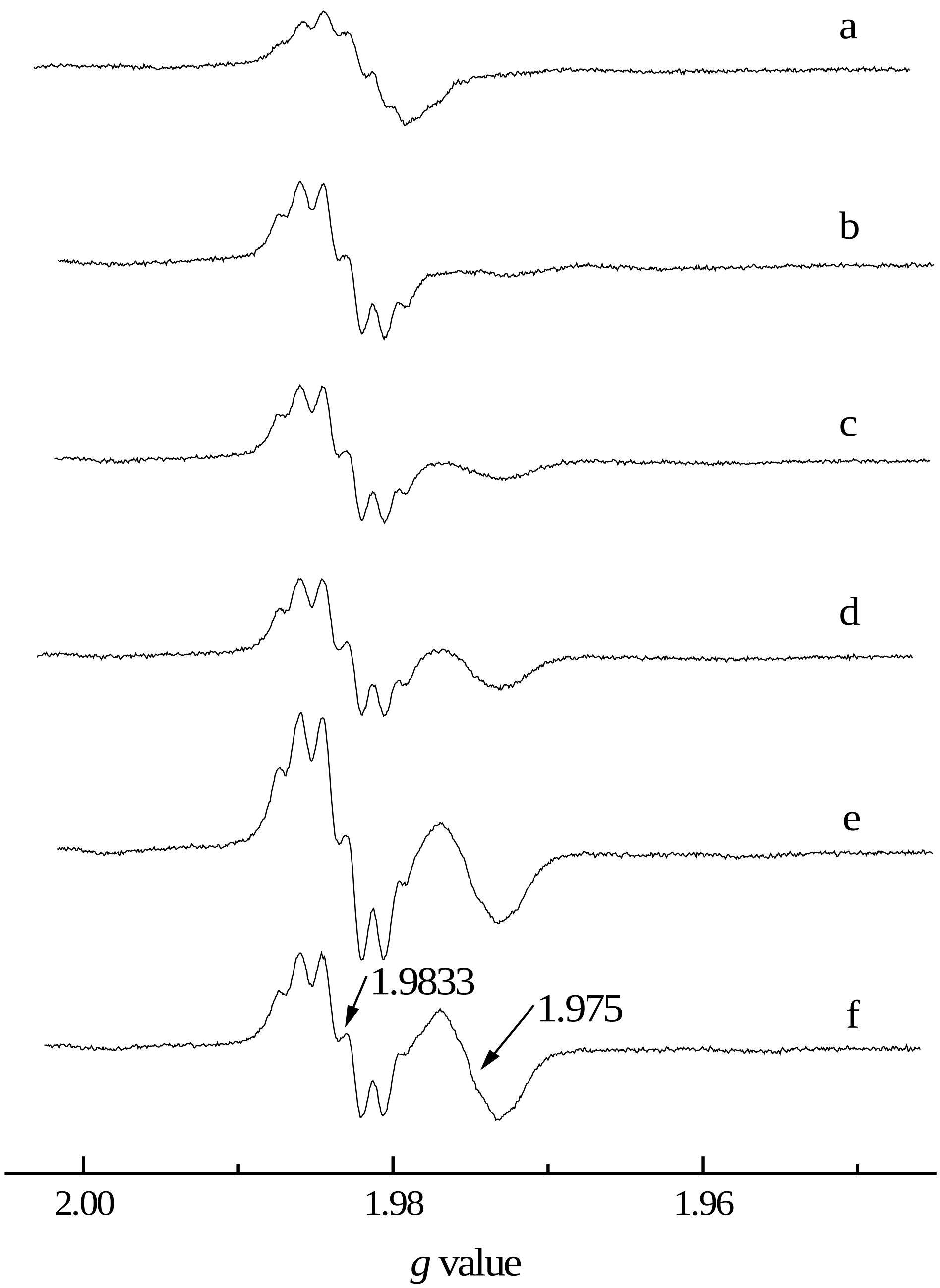

Figure S1. X-band EPR spectra of the Cr(V) products of the iodosobenzene oxidation of **1**.H_2O in acetonitrile recorded at: (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 60 min, and (f) 90 min after the addition of the oxidant.

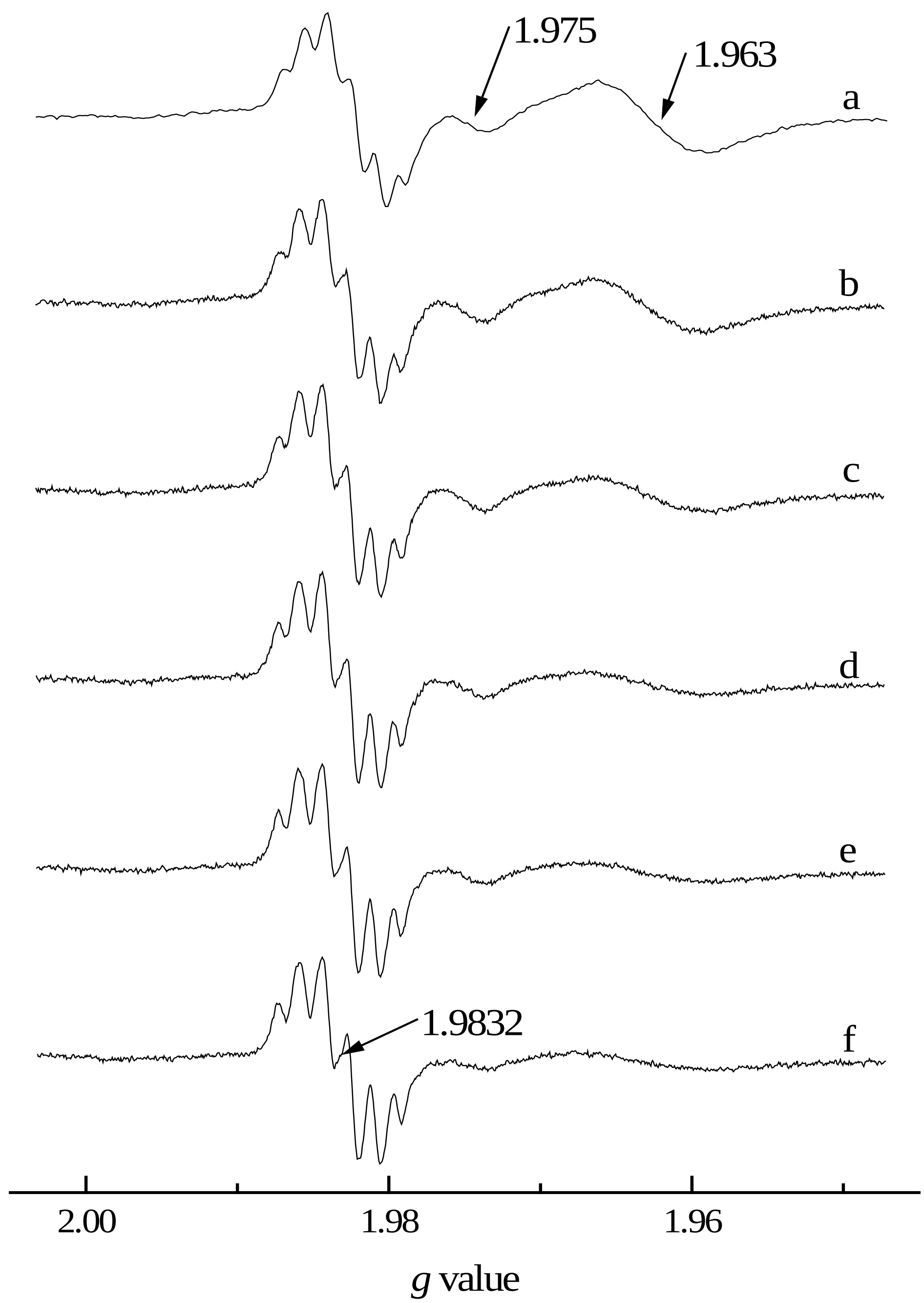

Figure S2. X-band EPR spectra of the Cr(V) products obtained during the *tert*-butylhydroperoxide oxidation of **1**.H_2O in acetonitrile recorded at: (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 60 min, and (f) 90 min after the addition of the oxidant.

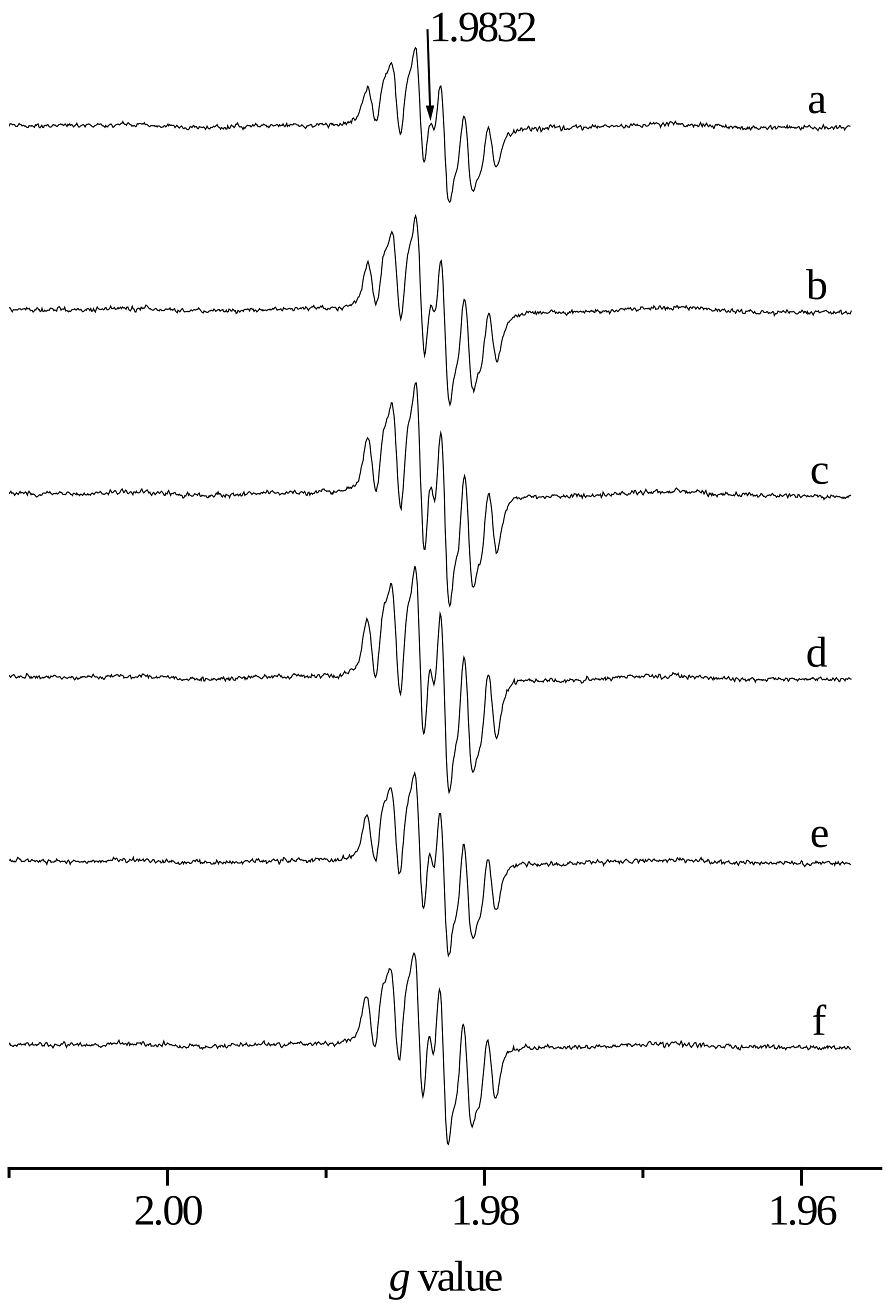

Figure S3 X-band EPR spectra of the Cr(V) products obtained during the iodosobenzene oxidation of **2** in DMF recorded at: (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 60 min, and (f) 90 min after the addition of the oxidant. Parameters: receiver gain, 6.32×10^4; sweep width, 100 G; power, 20.17 mW; modulation amplitude, 1.00 G; scans, 3.

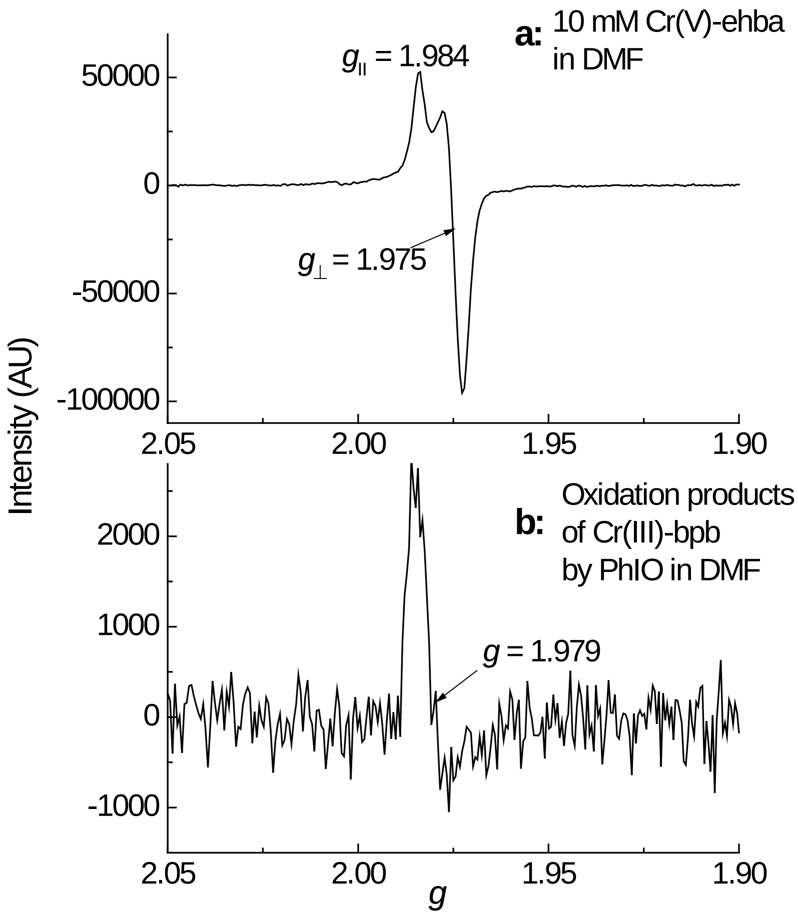

Figure S4 Low-temperature (~77 K) X-band EPR spectra of (a) Na[Cr^{V}O(ehba)$_2$] (10 mM in DMF) and (b) Oxidation of ~5 mg mL^{-1} of **1**.H_2O with ~20 mg of PhIO in DMF reacted for 10 min at ~25 ^{o}C. Modulation amplitude, 5.0 G.

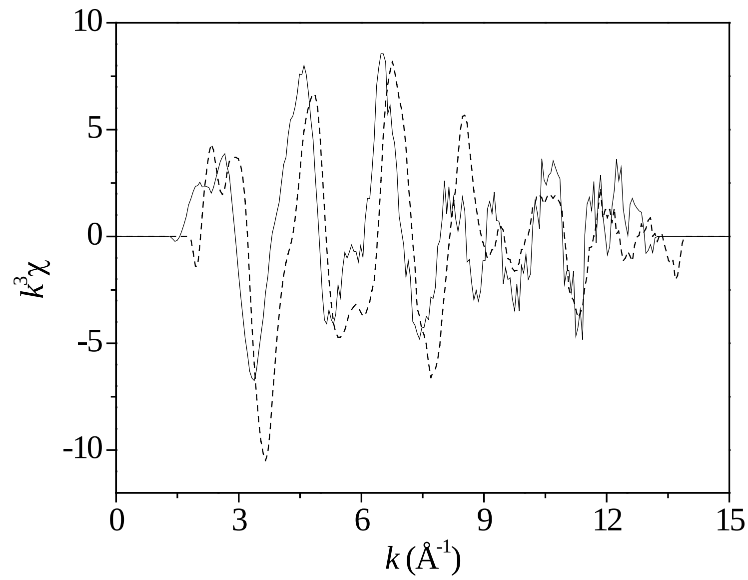

Figure S5 Observed EXAFS curves for **1**.DMF.0.5H_2O (solid line) and **2** (dashed line) showing the effect of substitution of the Cl^- axial ligand by a H_2O ligand.