Supplementary Information for Deprotonation of Water Ligands in V, Cr, Mn, Fe and Co Complexes Reduces Oxidation-driven Carboxylate Ligand Frequency Shifts

Wooi Yee Chuah, Terry J. Frankcombe
Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia
School of Physical, Environmental and Mathematical Sciences, University of New South Wales, Canberra, ACT 2600, Australia

Supporting Information

All frequency shift calculations performed in this study are shown below.

1V

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	CASSCF parameters
ωB97XD	1-	4	2				
	0	**3**	**3**	**-55**	**+39**	**1.08**	
	1-	3	3	-41	-1	1.59	
	1-	2	4	+14	-12	2.70	
M11L	1-	4	2				
	0	**3**	**3**	**-49**	**+27**	**1.13**	
	1-	3	3	-40	-11	1.90	
	1-	2	4	+15	-11	2.63	
M06L	1-	4	2				
	0	**3**	**3**	**-52**	**+40**	**0.94**	
	1-	3	3	-47	-7	1.55	
	1-	2	4	+28	-9	2.01	
CASSCF	1-	4	2				3 electrons, 5 orbitals
	0	**3**	**3**	**-68**	**+55**	**1.11**	2 electrons, 5 orbitals
	1-	3	3	-9	+8	0.97	2 electrons, 5 orbitals

2V

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	CASSCF parameters
ωB97XD	1+	7	2, 2				
	2+	**6**	**2, 3**	**-20**	**-29**	**8.43**	
	3+	**5**	**3, 3**	**-3**	**-80**	**14.03**	
	1+	6	2, 3	+2	-14	1.81	
	1+	5	3, 3	-1	-6	2.37	
	1+	4	3, 4	+2	-15	2.92	
	1+	3	4, 4	-10	-9	3.11	
M11L	1+	7	2, 2				
	2+	**6**	**2, 3**	**-14**	**-44**	**8.61**	
	3+	**5**	**3, 3**	**-1**	**-68**	**14.08**	
	1+	6	2, 3	0	-22	1.95	
	1+	5	3, 3	+5	+9	2.45	
	1+	4	3, 4	-1	-24	2.91	
	1+	3	4, 4	-4	-24	3.10	
M06L	1+	7	2, 2				
	2+	**6**	**2, 3**	**+8**	**-50**	**8.55**	
	3+	**5**	**3, 3**	**-11**	**-40**	**13.89**	
	1+	6	2, 3	+13	-12	1.76	
	1+	5	3, 3	-6	+4	2.10	
	1+	4	3, 4	-7	-35	2.42	
	1+	3	4, 4	+5	-17	2.58	
CASSCF	1+	7	2, 2				6 electrons, 6 orbitals
	2+	**6**	**2, 3**	**-8**	**-36**	**8.47**	5 electrons, 6 orbitals
	3+	**5**	**3, 3**	**-16**	**-84**	**13.99**	4 electrons, 6 orbitals
	1+	6	2, 3	0	-16	2.16	5 electrons, 6 orbitals
	1+	5	3, 3	-1	-33	2.77	4 electrons, 6 orbitals

1V_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)
ωB97XD	1-	4	2			
	0	**3**	**3**	**-117**	**+56**	**1.52**
	1-	3	3	-35	+7	1.75
	1-	2	4	-20	+1	2.77
M11L	1-	4	2			
	0	**3**	**3**	**-112**	**+42**	**1.53**
	1-	3	3	-31	+1	1.97
	1-	2	4	-14	-12	2.83
M06L	1-	4	2			
	0	**3**	**3**	**-122**	**+57**	**1.36**

	1-	3	3	-33	+5	1.64
	1-	2	4	-5	-10	2.24

2V_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)
ωB97XD	1-	7	2, 2			
	0	**6**	**2, 3**	**+2**	**-41**	**1.31**
	1+	**5**	**3, 3**	**-13**	**-42**	**6.73**
	1-	6	2, 3	+2	-7	1.38
	1-	5	3, 3	+2	-7	1.62
M11L	1-	7	2, 2			
	0	**6**	**2, 3**	**+25**	**-41**	**1.30**
	1+	**5**	**3, 3**	**-11**	**-50**	**6.66**
	1-	6	2, 3	+23	0	1.55
	1-	5	3, 3	+8	-3	1.79
M06L	1-	7	2, 2			
	0	**6**	**2, 3**	**+13**	**-36**	**1.29**
	1+	**5**	**2, 4**	**+14**	**-24**	**6.33**
	1-	6	2, 3	+16	-8	1.00
	1-	5	3, 3	+8	+5	1.90

1Cr

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)
ωB97XD	1-	5	2			
	0	**4**	**3**	**-61**	**+51**	**2.32**
	1+	**3**	**4**	**-150**	**+20**	**7.44**
	1-	4	3	-6	-8	2.52
	1-	3	4	-3	-3	2.97
M11L	1-	5	2			
	0	**4**	**3**	**-63**	**+50**	**1.47**
	1+	**3**	**4**	**-133**	**-16**	**7.37**
	1-	4	3	-4	-9	1.91
	1-	3	4	-2	-5	2.88
M06L	1-	5	2			
	0	**4**	**3**	**-67**	**+43**	**2.02**
	1+	**3**	**4**	**-302**	**+40**	**7.00**
	1-	4	3	-10	-6	2.14
	1-	3	4	+1	-1	2.36

2Cr

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	Comments
ωB97XD	1+	9	2, 2				
	2+	8	**2, 3**	**-16**	**-43**	**9.72**	
	3+	7	**3, 3**	**-10**	**-72**	**15.48**	
	1+	8	2, 3	-2	-16	2.92	
	1+	7	3, 3	-1	-20	3.36	
M11L	1+	9	2, 2				
	2+	8	**2, 3**	**-5**	**-63**	**9.48**	
	3+	7	**3, 3**	**-12**	**-51**	**14.78**	
	1+	8	2, 3	+3	-15	2.60	
	1+	7	3, 3	+2	-15	2.86	
M06L	1+	9	2, 2				
	2+	8	**2.5, 2.5**	**+3**	**-54**	**9.26**	Delocalised electron spin
	3+	7	**3, 3**	**-41**	**-76**	**15.30**	
	1+	8	2, 3	+1	-19	2.57	
	1+	7	3, 3	0	-23	3.01	

1Cr_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	Comments
ωB97XD	1-	3	2				
	0	4	**3**	**-72**	**+44**	**2.32**	
	1-	4	3	-5	+5	2.52	
	1-	3	4	-5	-13	2.97	
M11L	1-	3	2				
	0	4	**3**	**-62**	**+38**	**1.47**	
	1-	4	3	+2	+6	1.91	
	1-	3	4	-7	-11	2.88	
M06L	1-	3	2				
	0	4	**3**	**-70**	**+47**	**2.02**	

	1+	3	**4**	**-290**	**+37**	**7.00**	Formate H-bonds water with
	1-	4	3	-17	+9	2.14	other methods
	1-	3	4	+14	-15	2.36	

2Cr_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	Comments
ωB97XD	1-	5	2, 2				
	0	6	**2, 3**	**+5**	**-32**	**1.19**	
	1+	7	**3, 3**	**-2**	**-25**	**5.74**	
	1-	6	2, 3	+16	+1	0.91	
	1-	7	3, 3	+3	-3	1.45	
M11L	1-	5	2, 2				
	0	6	**2.5, 2.5**	**+10**	**-48**	**1.27**	Delocalised electron spin
	1+	7	**3, 3**	**-8**	**-7**	**6.20**	
	1-	6	2, 3	+7	-15	1.44	
	1-	7	3, 3	+13	+22	1.82	
M06L	1-	5	2, 2				
	0	6	**2.5, 2.5**	**+43**	**-38**	**0.60**	Delocalised electron spin
	1+	7	**3, 3**	**-9**	**-5**	**5.56**	
	1-	6	2, 3	+28	-12	0.51	
	1-	7	3, 3	+26	+22	0.92	

1Mn

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)
ωB97XD	0	6	2			
	1+	5	**3**	**-112**	**+40**	**7.04**
	0	5	3	-46	-5	3.18
	0	4	4	-10	+19	4.25
M11L	0	6	2			
	1+	5	**3**	**-108**	**+17**	**6.41**
	0	5	3	-55	-16	2.57
	0	4	4	-7	+12	3.28
M06L	0	6	2			
	1+	5	**3**	**-125**	**+9**	**6.78**
	0	5	3	-60	-15	2.83
	0	4	4	-29	+8	3.57

2Mn

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)
ωB97XD	1+	11	2, 2			
	2+	10	**2, 3**	**-33**	**-5**	**9.67**
	3+	9	**3, 3**	**+13**	**-96**	**15.46**
	1+	10	2, 3	+8	-6	3.09
	1+	9	3, 3	+7	-3	3.51
M11L	1+	11	2, 2			
	2+	10	**2, 3**	**-41**	**-16**	**9.10**
	3+	9	**3, 3**	**+21**	**-86**	**14.67**
	1+	10	2, 3	+6	-5	2.41
	1+	9	3, 3	+8	-3	2.65
M06L	1+	11	2, 2			
	2+	10	**2, 3**	**-48**	**-20**	**9.38**
	3+	9	**3, 3**	**+4**	**-91**	**15.03**
	1+	10	2, 3	+2	-13	2.66
	1+	9	3, 3	+4	-4	3.00

1Mn_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	Comments
ωB97XD	1-	2	2				
	0	3	**3**	**-80**	**+49**	**1.85**	
	1-	3	3	-15	-5	2.12	
	1-	4	4	-16	+6	2.95	
M11L	1-	2	2				
	0	3	**3**	**-87**	**+34**	**2.11**	
	1-	3	3	-22	-15	2.62	
	1-	4	4	-24	+3	3.11	
M06L	1-	2	2				
	0	3	**3**	**-83**	**+45**	**1.37**	
	1+	4	**4**	**-184**	**+2**	**7.53**	Formate interacts with water
	1-	3	3	-11	-9	1.63	with other methods

	1-	4	4	-18	+4	2.04	

2Mn_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	Comments
ωB97XD	1-	3	2, 2				
	0	4	**2, 3**	**-12**	**-20**	**2.45**	
	1+	5	**3, 3**	**+1**	**-60**	**6.72**	
	1-	4	2, 3	-2	-4	2.16	
	1-	5	3, 3	+5	-7	2.13	
M11L	1-	3	2, 2				
	0	4	**2, 3**	**+19**	**-52**	**2.47**	
	1+	5	**3, 3**	**-25**	**-24**	**7.15**	
	1-	4	2, 3	+6	-10	2.39	
	1-	5	3, 3	+2	+9	2.72	
M06L	1-	3	2, 2				
	0	4	**2.5, 2.5**	**-4**	**-30**	**1.71**	Electron spin delocalised
	1+	5	**3, 3**	**-40**	**-43**	**6.56**	
	1-	4	2, 3	+5	-11	1.54	
	1-	5	3, 3	-3	+7	1.81	

1Fe_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	Comments
ωB97XD	1-	1	2				Formate extracts a H from water
	0	**2**	**3**	**-98**	**+54**	**2.56**	in the second direct ox.
	1-	2	3	-26	-4	2.71	
	1-	3	4	+1	+21	3.68	
M11L	1-	1	2				
	0	**2**	**3**	**-90**	**+34**	**2.75**	
	1+	**3**	**4**	**-355**	**-136**	**9.21**	
	1-	2	3	-29	-16	3.27	
	1-	3	4	-21	-3	3.89	
M06L	1-	1	2				
	0	**2**	**3**	**-99**	**+45**	**2.17**	
	1+	**3**	**4**	**-249**	**+8**	**8.20**	
	1-	2	3	-22	-8	2.35	
	1-	3	4	+5	+19	2.91	

2Fe_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)	Comments
ωB97XD	1-	1	2, 2				
	0	**2**	**2, 3**	**+3**	**-16**	**2.25**	
	1+	**3**	**3, 3**	**-24**	**-55**	**7.72**	
	1-	2	2, 3	+3	-6	2.47	
	1-	3	3, 3	+1	-10	3.01	
M11L	1-	1	2, 2				
	0	**2**	**2.5, 2.5**	**+22**	**-47**	**2.84**	Delocalised electron spin
	1+	**3**	**3, 3**	**-27**	**-25**	**7.94**	
	1-	2	2, 3	+9	-5	3.17	
	1-	3	3, 3	+5	-8	3.42	
M06L	1-	1	2, 2				
	0	**2**	**2.5, 2.5**	**+26**	**-23**	**2.04**	Delocalised electron spin
	1+	**3**	**3, 3**	**-34**	**-18**	**7.58**	
	1-	2	2, 3	+15	0	2.21	
	1-	3	3, 3	+1	-3	2.73	

1Co_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)
ωB97XD	1-	2	2			
	0	**1**	**3**	**-56**	**+47**	**3.46**
	1-	1	3	-11	-15	3.55
	1-	2	4	-5	+6	4.19
M11L	1-	2	2			
	0	**1**	**3**	**-45**	**+35**	**2.35**
	1-	1	3	-5	-24	2.62
	1-	2	4	-10	+5	4.36
M06L	1-	2	2			
	0	**1**	**3**	**-52**	**+38**	**2.85**
	1-	1	3	-5	-21	2.93

	1-	2	4	-1	+4	3.52

2Co_CN

Method	Charge	Multiplicity	Oxidation State	ΔSymm (cm^{-1})	ΔASymm (cm^{-1})	ΔE (eV)
ωB97XD	1-	3	2, 2			
	0	**2**	**2, 3**	**-34**	**-5**	**3.69**
	1+	**1**	**3, 3**	**+4**	**-42**	**8.32**
	1-	2	2, 3	+4	+1	3.62
	1-	1	3, 3	+6	-4	4.08
M11L	1-	3	2, 2			
	0	**2**	**2, 3**	**-31**	**-20**	**2.70**
	1+	**1**	**3, 3**	**+8**	**-26**	**7.23**
	1-	2	2, 3	+9	+6	3.04
	1-	1	3, 3	+1	-7	3.15
M06L	1-	3	2, 2			
	0	**2**	**2, 3**	**-5**	**-36**	**3.11**
	1+	**1**	**3, 3**	**-37**	**-13**	**7.80**
	1-	2	2, 3	+2	-5	3.17
	1-	1	3, 3	+5	-1	3.43