Electronic Supporting Information for

Molybdenum(VI) tris(amidophenoxide) complexes

Alexander N. Erickson and Seth N. Brown*

251 Nieuwland Science Hall
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556-5670 USA
E-mail: Seth.N.Brown.114@nd.edu

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I. X-ray Crystallography

Crystallography of [(^{H}ap)(^{H}apH)MoO]$_2$(μ-O)•C_7D_8 and [(^{PhCH2}ap)(^{PhCH2}apH)MoO]$_2$(μ-O)•C_7H_8. Crystals of [(^{H}ap)(^{H}apH)MoO]$_2$(μ-O)•C_7D_8 were deposited from the reaction mixture of (^{H}ap)H_2 with $MoO_2(acac)_2$ in toluene-d_8 after evaporation of the solvent, dissolution of the residue in hexanes and standing of the hexane solution for 3 months at room temperature. The structure was solved using direct methods. Hydrogen atoms were found and refined for the metal complex and placed in calculated positions for toluene-d_8.

Crystals of [(^{PhCH2}ap)(^{PhCH2}apH)MoO]$_2$(μ-O)•C_7H_8 were deposited from the reaction mixture of (^{PhCH2}ap)H_2 with $MoO_2(acac)_2$ in toluene after layering with acetonitrile. The structure was solved using direct methods. One of the benzyl groups (attached to C84) was disordered in two orientations. The phenyl rings of these two orientations were constrained as rigid hexagons, with the thermal parameters of corresponding atoms in the two orientations constrained to be equal while the occupancies of the groups were allowed to refine (the occupancy of the major orientation refined to 0.640(4). The program SQUEEZE[S1] was used to remove undifferentiated disordered solvent. The analysis revealed that there were 110 electrons per unit cell, which was assigned as one toluene per formula unit. All hydrogen atoms were placed in calculated positions.

Table S1. Crystallographic details for $[(^{H}ap)(^{H}apH)MoO]_2(\mu\text{-}O)\bullet C_7D_8$ and $[(^{PhCH2}ap)(^{PhCH2}apH)MoO]_2(\mu\text{-}O)\bullet C_7H_8$.

	$[(^{H}ap)(^{H}apH)MoO]_2(\mu\text{-}O)\bullet C_7D_8$	$[(^{PhCH2}ap)(^{PhCH2}apH)MoO]_2(\mu\text{-}O)\bullet C_7H_8$
Molecular formula	$C_{87}H_{102}D_8Mo_2N_4O_7$	$C_{115}H_{134}Mo_2N_4O_7$
Formula weight	1523.71	1876.13
T/K	120(2)	120(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
λ/Å	0.71073 (Mo *K*α)	0.71073 (Mo *K*α)
Total data collected	154868	121030
No. of indep reflns.	19803	24909
R_{int}	0.0305	0.0621
Obsd refls [$I > 2\sigma(I)$]	16394	17856
a/Å	16.4155(8)	15.1553(8)
b/Å	23.0354(11)	15.2866(8)
c/Å	22.6673(11)	23.9707(12)
α/°	90	75.3310(16)
β/°	109.0155(15)	79.4159(17)
γ/°	90	72.7891(16)
V/Å^3	8103.6(7)	5096.1(5)
Z	4	2
μ/mm^{-1}	0.364	0.303
Crystal size/mm	0.38 × 0.29 × 0.16	0.37 × 0.17 × 0.13
No. refined params	1310	1088
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0313, 0.0730	0.0641, 0.1577
$R1$, $wR2$ [all data]	0.0450, 0.0808	0.0971, 0.1721
Goodness of fit	1.070	1.085

Figure S1. Thermal ellipsoid plot of [(^{H}ap)(^{H}apH)MoO]$_2$(μ-O)•C_7D_8. Hydrogen atoms attached to carbon atoms and solvent have been omitted for clarity.

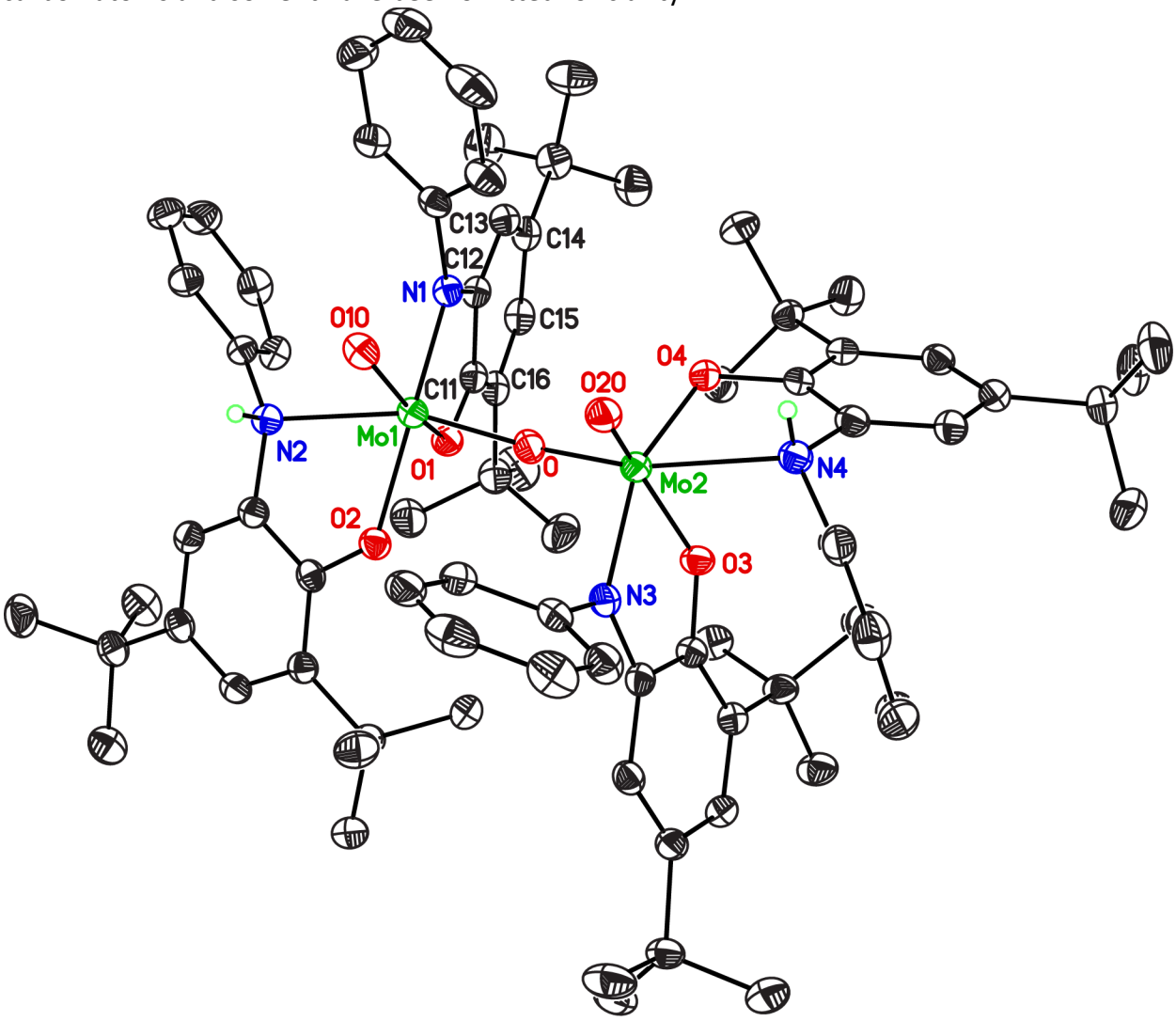


Figure S2. Thermal ellipsoid plot of [(^{PhCH2}ap)(^{PhCH2}apH)MoO]$_2$(μ-O)•C_7H_8. Hydrogen atoms attached to carbon atoms, phenyl rings that are part of benzyl groups and toluene solvent have been omitted for clarity.

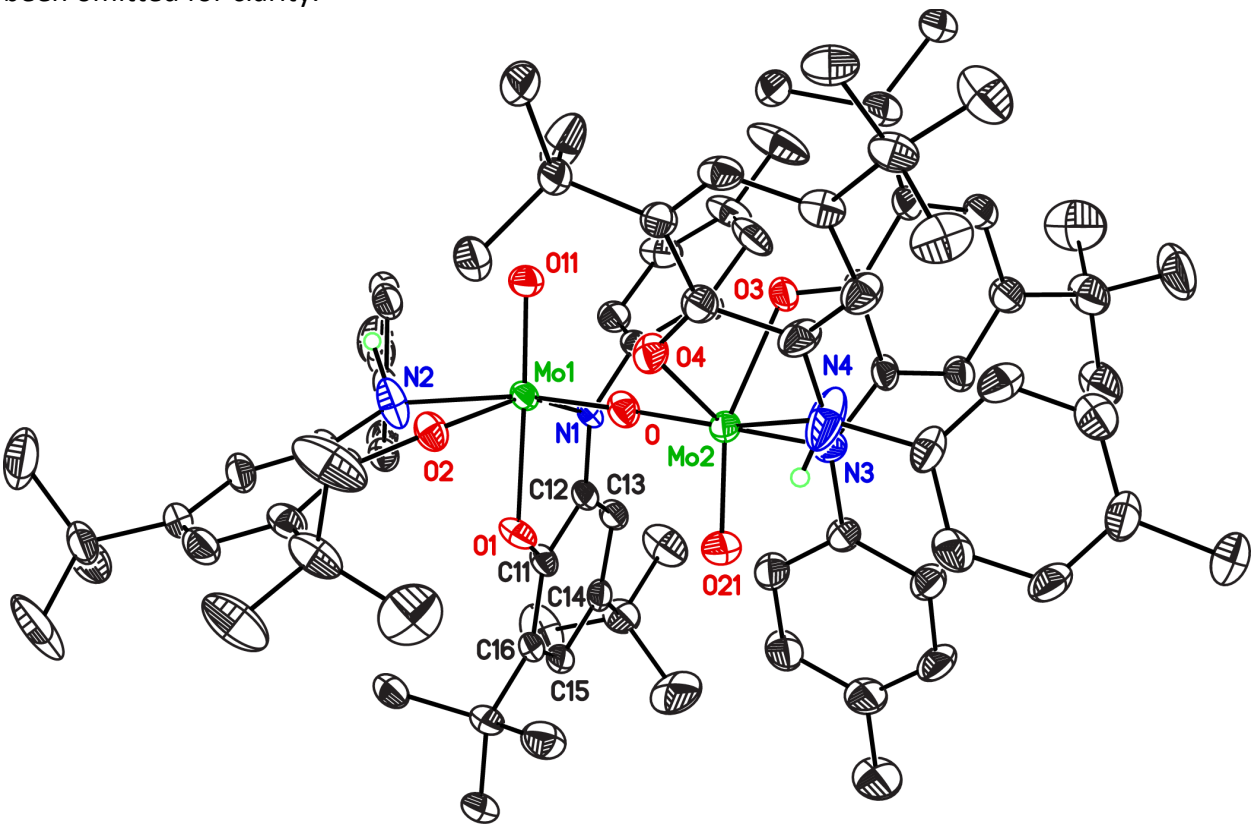


Table S2. Selected bond distances (Å), angles (°), and MOS values for [(^{H}ap)(^{H}apH)MoO]$_2$(μ-O)•C_7D_8 and [(^{PhCH2}ap)(^{PhCH2}apH)MoO]$_2$(μ-O)•C_7H_8. Numbering scheme given is for species bonded to Mo1 in the ^{H}ap structure, with analogous values for Mo2 and for the ^{PhCH2}ap structure listed in the corresponding column.

	[(^{H}ap)(^{H}apH)MoO]$_2$(μ-O)•C_7D_8		[(^{PhCH2}ap)(^{PhCH2}apH)MoO]$_2$(μ-O)•C_7H_8	
Parameter	Mo1	Mo2	Mo1	Mo2
Mo–O10	1.6884(13)	1.6975(12)	1.695(3)	1.690(3)
Mo–O1	2.0347(12)	2.0266(12)	2.056(3)	2.045(3)
Mo–O2	1.9675(12)	1.9679(13)	1.989(3)	1.984(3)
Mo–N1	2.0297(15)	2.0285(15)	2.040(3)	2.036(3)
Mo–N2	2.3126(15)	2.3631(16)	2.200(3)	2.248(4)
Mo–O	1.8819(13)	1.8571(13)	1.877(3)	1.865(3)
O1–C11	1.320(2)	1.326(2)	1.314(4)	1.313(4)
N1–C12	1.379(2)	1.381(2)	1.384(5)	1.374(5)
C11–C12	1.408(2)	1.402(3)	1.406(5)	1.414(5)
C12–C13	1.397(3)	1.401(3)	1.386(5)	1.399(5)
C13–C14	1.375(3)	1.375(3)	1.382(5)	1.373(6)
C14–C15	1.410(3)	1.408(3)	1.409(6)	1.402(5)
C15–C16	1.377(3)	1.383(3)	1.372(5)	1.376(5)
C11–C16	1.409(2)	1.408(3)	1.415(5)	1.408(5)
MOS[S2]	–1.44(10)	–1.51(10)	–1.45(14)	–1.39(10)
O10-Mo-O	102.31(6)	101.72(6)	101.00(12)	101.44(13)
O10-Mo-O1	156.95(6)	157.21(6)	159.89(12)	157.98(12)
O10-Mo-O2	109.08(6)	109.92(6)	90.55(11)	111.94(13)
O10-Mo-N1	87.59(6)	89.05(6)	89.63(12)	88.98(13)
O10-Mo-N2	85.21(6)	83.13(6)	89.60(14)	86.91(16)
O-Mo-O1	95.29(5)	96.90(5)	93.47(11)	95.29(11)
O-Mo-O2	88.51(5)	89.85(5)	90.55(11)	89.14(11)
O-Mo-N1	98.99(6)	100.46(6)	100.82(12)	99.63(12)
O-Mo-N2	162.63(5)	163.24(6)	163.77(13)	162.51(12)
O1-Mo-O2	85.92(5)	82.95(5)	81.70(11)	82.27(11)
O1-Mo-N1	74.94(5)	74.65(5)	73.87(11)	74.07(11)
O1-Mo-N2	82.17(5)	82.77(5)	79.62(14)	81.07(16)
O2-Mo-N1	159.95(6)	156.24(6)	153.52(11)	155.37(12)
O2-Mo-N2	74.19(5)	73.46(5)	74.02(12)	73.45(12)
N1-Mo-N2	96.93(6)	95.62(6)	91.41(13)	95.82(14)
Mo-N1-C12	118.67(12)	118.99(12)	119.3(2)	119.5(2)
Mo-N1-C101	123.70(11)	121.90(12)	120.9(2)	121.4(2)
C12-N1-C101	117.33(15)	118.72(15)	119.7(3)	119.1(3)
Mo-N2-C22	106.85(11)	105.72(11)	113.7(3)	110.7(3)
Mo-N2-C201	118.38(11)	117.24(11)	122.4(2)	119.6(3)
C22-N2-C201	116.98(14)	116.57(15)	121.9(3)	121.1(4)
Mo1-O-Mo2	165.10(8)		178.33(17)	

Figure S3. Thermal ellipsoid plot (50% ellipsoids) of (^{tBu2}ap)$_3$Mo•CDCl$_3$•2.5 CH$_3$CN. Hydrogen atoms and lattice solvent are omitted for clarity.

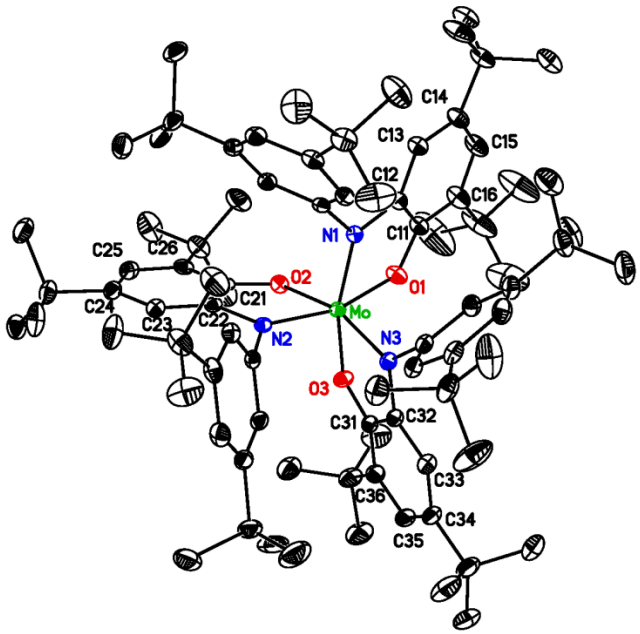


Figure S4. Thermal ellipsoid plot (50% ellipsoids) of (^{CH3O}ap)$_3$Mo•0.67 CH$_3$CN. Hydrogen atoms and lattice solvent are omitted for clarity.

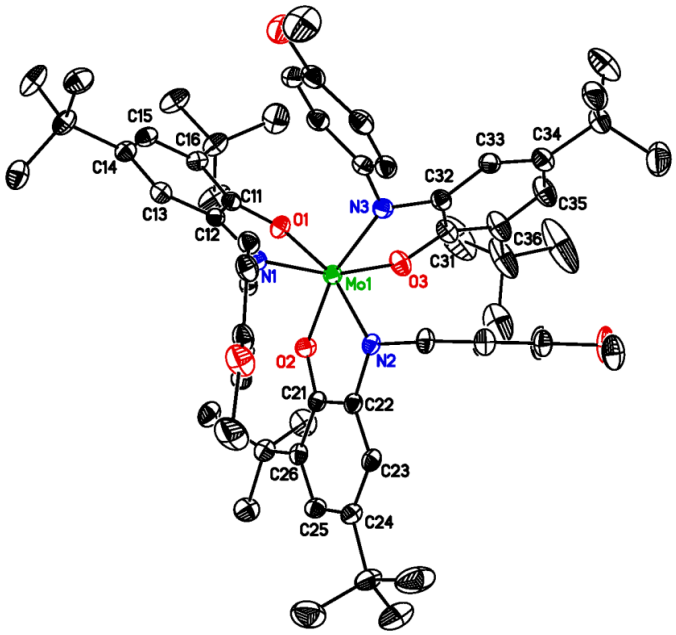
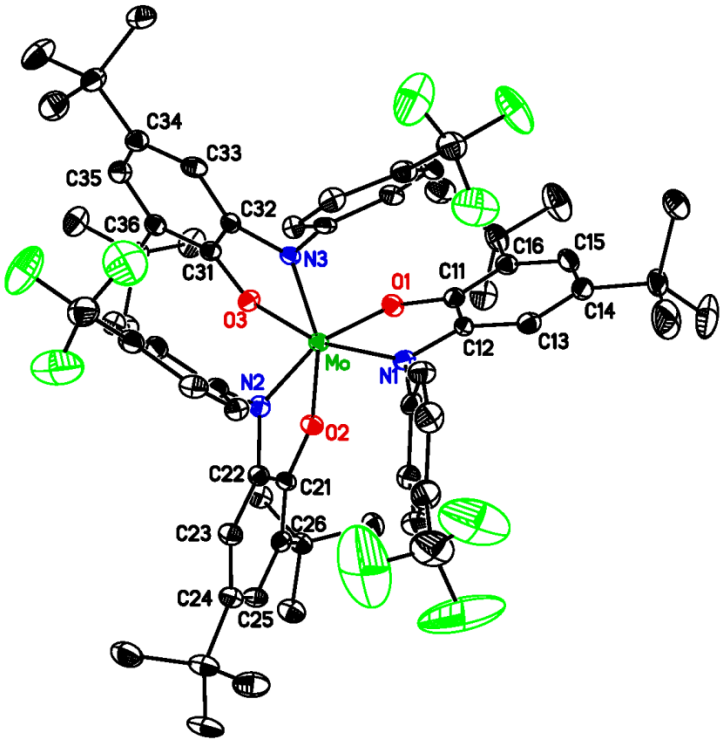


Figure S5. Thermal ellipsoid plot (50% ellipsoids) of (^{CF3}ap)$_3$Mo•2.5 $CHCl_3$•CH_3CN. Hydrogen atoms and lattice solvent are omitted for clarity.



II. UV-Vis Spectra

Figure S6. UV-Vis spectrum of (^{CH3O}ap)$_3$Mo (3.1×10^{-5} M, CH_2Cl_2).

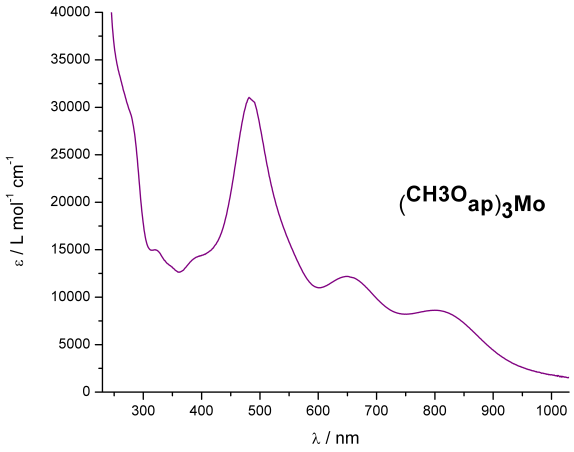


Figure S7. UV-Vis spectrum of ($^{t\text{Bu}2}$ap)$_3$Mo (2.4×10^{-5} M, CH_2Cl_2).

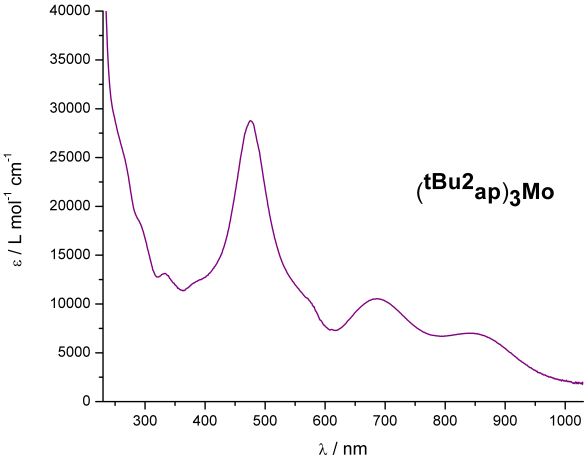


Figure S8. UV-Vis spectrum of (^{PhCH2}ap)$_3$Mo (2.3×10^{-5} M, CH_2Cl_2).

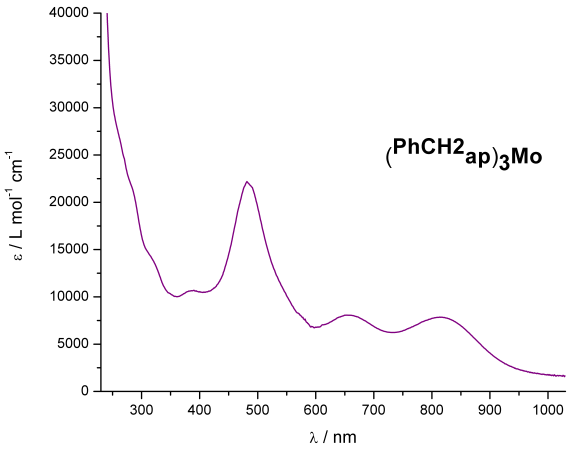


Figure S9. UV-Vis spectrum of (^{CF3}ap)$_3$Mo (2.7×10^{-5} M, CH_2Cl_2).

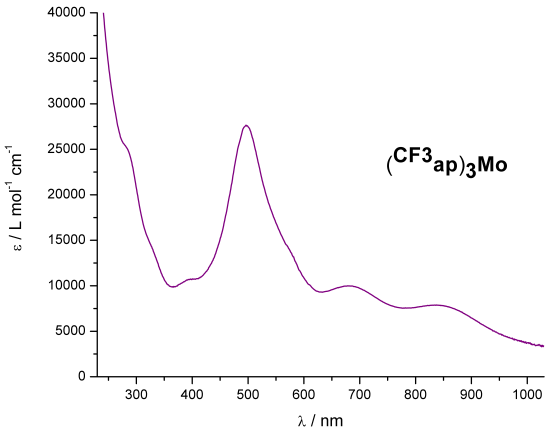


Figure S10. UV-Vis spectrum of ^{H}iq (1.7×10^{-4} M, CH_2Cl_2).

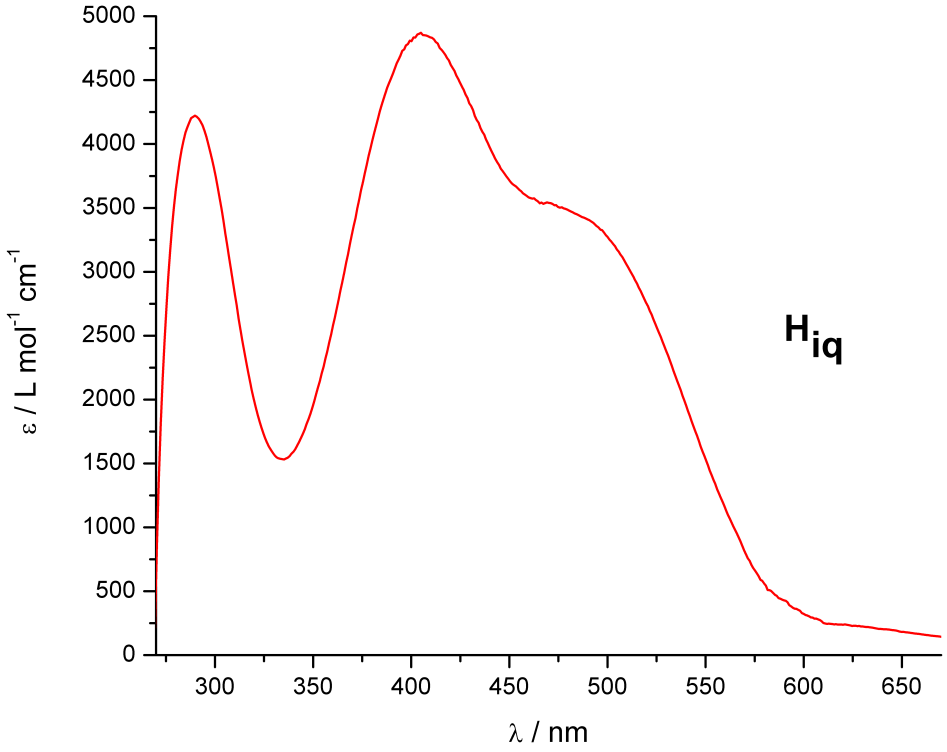
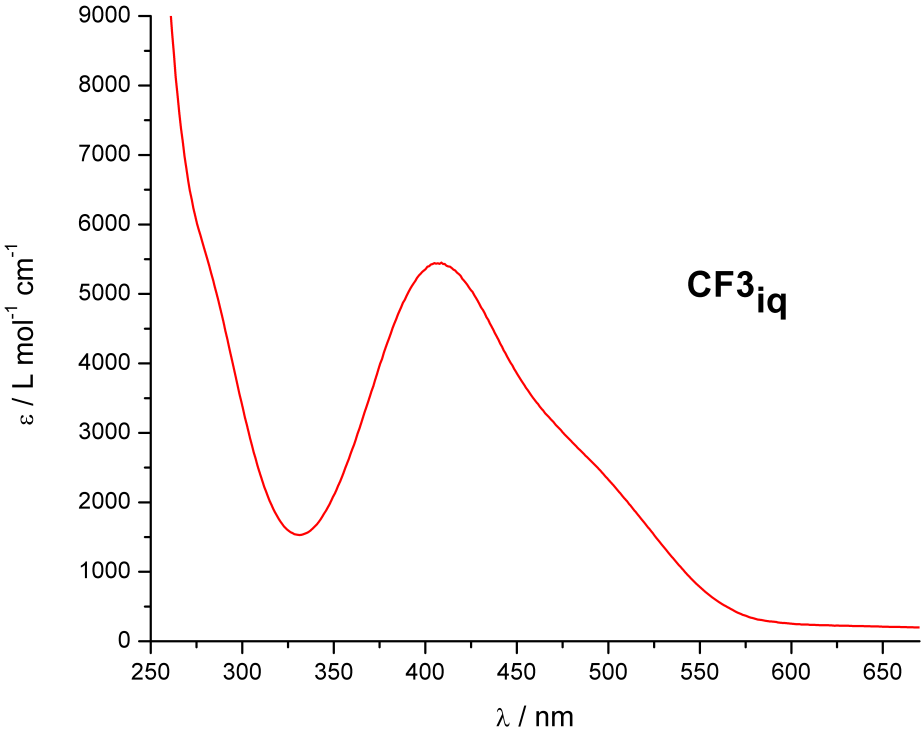
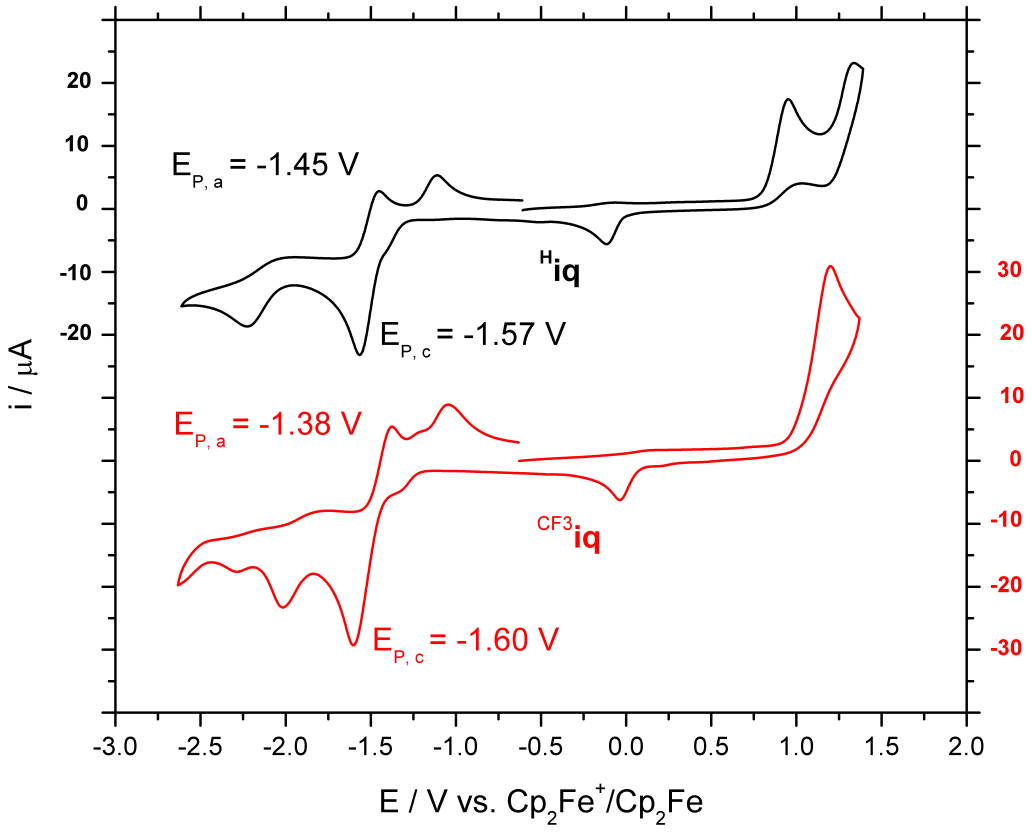


Figure S11. UV-Vis spectrum of ^{CF3}iq (1.5×10^{-4} M, CH_2Cl_2).



III. Electrochemistry

Figure S12. Cyclic voltammogram of iminoquinones ^{H}iq and ^{CF3}iq in CH_2Cl_2 (0.1 M Bu_4NPF_6, 60 mV s^{-1}).



IV. Variable-Temperature NMR Spectra

Figure S13. Variable-temperature ^{1}H NMR spectra of hydrolysis product [(^{H}ap)(^{H}apH)MoO]$_2$(μ-O) (CD_2Cl_2, 500 MHz).

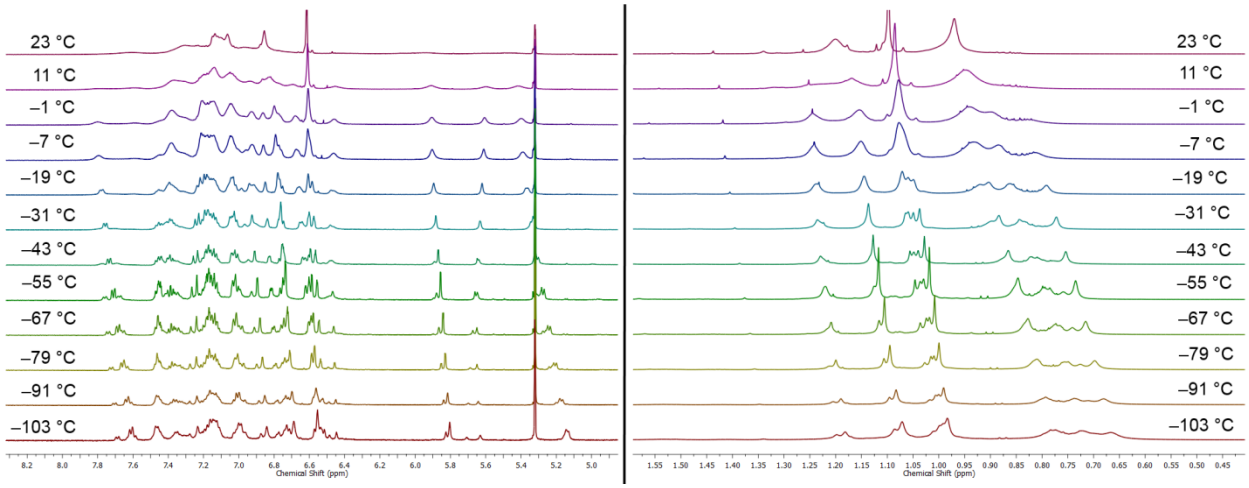


Figure S14. Variable-temperature ^{1}H NMR spectra of (^{H}ap)$_3$Mo (toluene-d_8, 500 MHz).

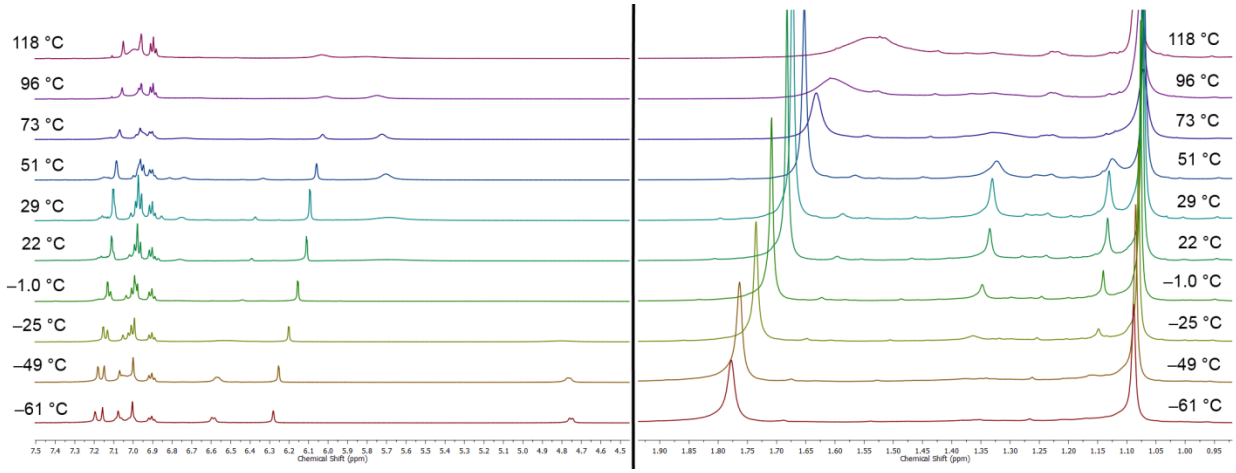


Figure S15. Variable-temperature ^{1}H NMR spectra of (^{CH3O}ap)$_3$Mo (toluene-d_8, 400 MHz).

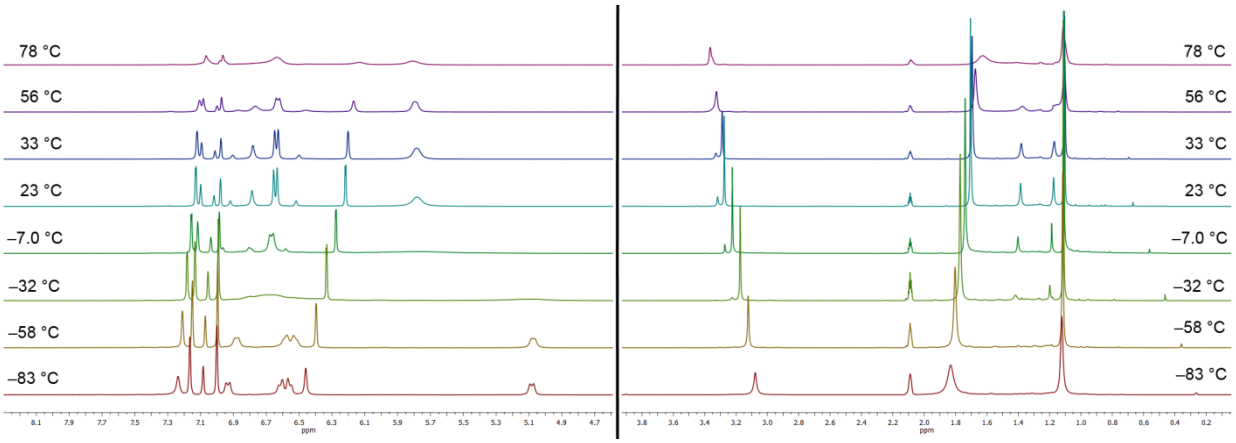


Figure S16. Variable-temperature ^{1}H NMR spectra of (^{PhCH2}ap)$_3$Mo (toluene-d_8, 400 MHz).

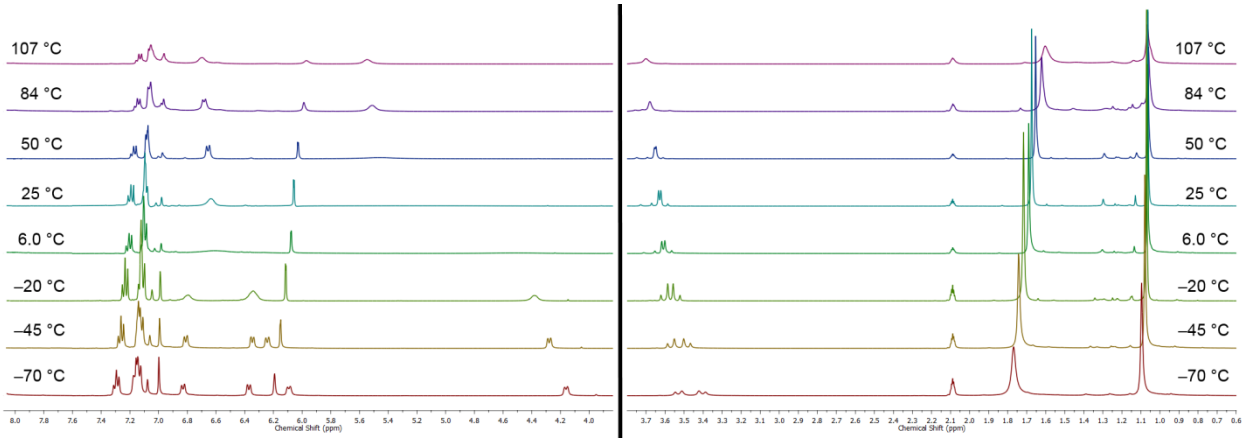


Figure S17. Variable-temperature ^{1}H NMR spectra of (^{CF3}ap)$_3$Mo (toluene-d_8, 400 MHz).

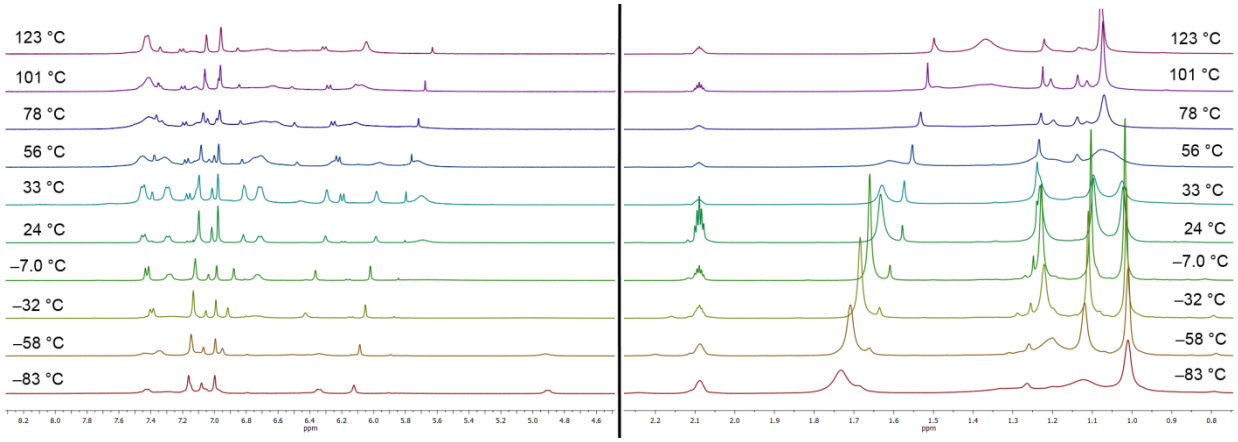
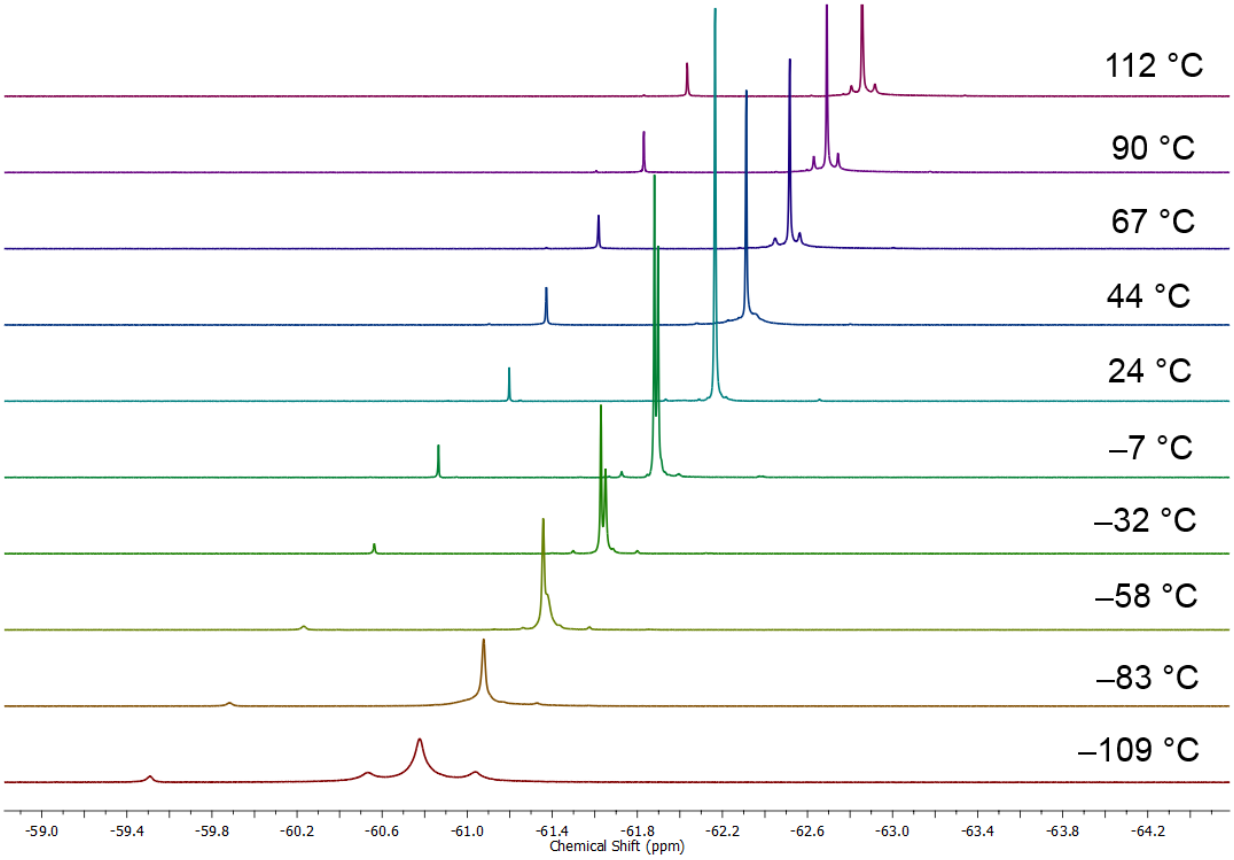


Figure S18. Variable-temperature ^{19}F NMR spectra of (^{CF3}ap)$_3$Mo (toluene-d_8, 400 MHz, in ppm downfield of $CFCl_3$).



V. DFT Calculations

fac-(ap)$_3$Mo E = –1846.34503563 a.u.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	42	0.000914	0.000899	-1.193151
2	8	-0.990875	-1.323135	-2.353585
3	7	-1.709420	-0.360239	-0.140636
4	8	1.643347	-0.196742	-2.354648
5	7	1.168934	-1.296149	-0.139497
6	8	-0.646440	1.522307	-2.356289
7	7	0.538778	1.661185	-0.138930
8	6	-2.106552	-1.866214	-1.883827
9	6	-2.529989	-1.388322	-0.613857
10	6	-3.700928	-1.900036	-0.028690
11	1	-4.033724	-1.537076	0.937210
12	6	-4.426953	-2.876522	-0.705793
13	1	-5.332470	-3.275493	-0.258040
14	6	-4.005101	-3.341407	-1.961803
15	1	-4.587578	-4.099993	-2.477610
16	6	-2.852574	-2.837310	-2.561796
17	1	-2.516823	-3.177331	-3.536328
18	6	2.672688	-0.887638	-1.882052
19	6	2.470624	-1.490619	-0.610815
20	6	3.500324	-2.244409	-0.022055
21	1	3.352234	-2.711188	0.945260
22	6	4.710086	-2.383969	-0.697391
23	1	5.509523	-2.965094	-0.247048
24	6	4.901593	-1.789499	-1.955018
25	1	5.850611	-1.913973	-2.469481
26	6	3.887809	-1.047380	-2.558292
27	1	4.014476	-0.588967	-3.533930
28	6	-0.564356	2.759120	-1.882807
29	6	0.056908	2.885668	-0.610623
30	6	0.193596	4.154059	-0.021138
31	1	0.670733	4.258898	0.946763
32	6	-0.290199	5.271603	-0.696533
33	1	-0.187605	6.254344	-0.245624
34	6	-0.899331	5.140313	-1.954850
35	1	-1.266146	6.024397	-2.469276
36	6	-1.033605	3.891384	-2.558907
37	1	-1.492848	3.772121	-3.535081
38	6	-2.183929	0.363865	1.004003
39	6	-2.113913	-0.197713	2.286455
40	1	-1.687098	-1.186061	2.416083
41	6	-2.586324	0.521641	3.385631
42	1	-2.524874	0.081269	4.377317
43	6	-3.131885	1.796664	3.216104
44	1	-3.498064	2.353062	4.074536
45	6	-3.210839	2.349074	1.935509
46	1	-3.639008	3.337205	1.791435
47	6	-2.743726	1.636241	0.829773
48	1	-2.812378	2.054963	-0.168471
49	6	0.776534	-2.075337	1.000133

50	6	1.214216	-1.733519	2.287055
51	1	1.847728	-0.864207	2.424090
52	6	0.825624	-2.509404	3.380662
53	1	1.165874	-2.236170	4.376008
54	6	0.005877	-3.626399	3.200825
55	1	-0.294146	-4.227370	4.054872
56	6	-0.419686	-3.970914	1.915690
57	1	-1.052322	-4.841092	1.763858
58	6	-0.034059	-3.202936	0.815509
59	1	-0.351575	-3.471227	-0.186426
60	6	1.406321	1.709533	1.003443
61	6	2.788251	1.567359	0.822877
62	1	3.181427	1.425011	-0.178003
63	6	3.643344	1.614517	1.925323
64	1	4.713293	1.498531	1.776214
65	6	3.129262	1.811868	3.209096
66	1	3.797376	1.850206	4.065086
67	6	1.751942	1.967164	3.385023
68	1	1.342829	2.125663	4.379336
69	6	0.888471	1.918523	2.289059
70	1	-0.181237	2.034478	2.423672

VI. References

(S1) P. van der Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A46**, 194-201.

(S2) S. N. Brown, *Inorg. Chem.*, 2012, **51**, 1251-1260.