Supporting Information

For

Determination of the Cu(III)-OH Bond Distance by Resonance Raman Spectroscopy using a Normalized Version of Badger's Rule

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Cross Validation. A 5-fold cross validation method was used to ensure the predictive power of the Badger's fit in Figure 3c.[1] All the data (bond length and normalized frequency, ν_μ) from Tables S3-S7 was collected into one master table. The data was randomly sorted into 5 equal groups. One group was selected as the 'test set' while the remaining four groups were used as the 'training set' where this data was fit using the Badger's rule equation (eq. 4). The obtained fitting equation was used to predict the bond length of the 'test set' data. This process was repeated so that each of the five groups became the 'test set'. Of the five 'training sets', the average value of C_{ij} was 182.3±0.5, while d_{ij} was 0.257±0.002. The root mean squared error (RMSE) was calculated for all data when it was designated the 'test set'. The obtained RMSE was 0.03 Å, which is the exact same value as calculated for the fitting of the entire data set, indicating that this correlation has excellent predictive power.

Bond Valence Sum Analysis

$$\text{Bond Valence} = e^{((R_0-R)/B)} \quad \text{(S1)}$$

Bond Valence Sum (BVS) equation used in Table 3, where R is the bond distance and R_0 and B are parameters specific to the bond of interest. The calculated bond valences are summed together to determine oxidation state of the metal center.[2]

Table S1. Calculated reduced masses used in this work (from unitless relative atomic masses).

Atomic Pair	Reduced Mass (μ)
N-N	7.0
O-O	8.0
S-S	16.0
Cr-O	12.2
Mn-O	12.4
Mn-N	11.2
Fe-O	12.4
Fe-N	11.2
Cu-O	12.8

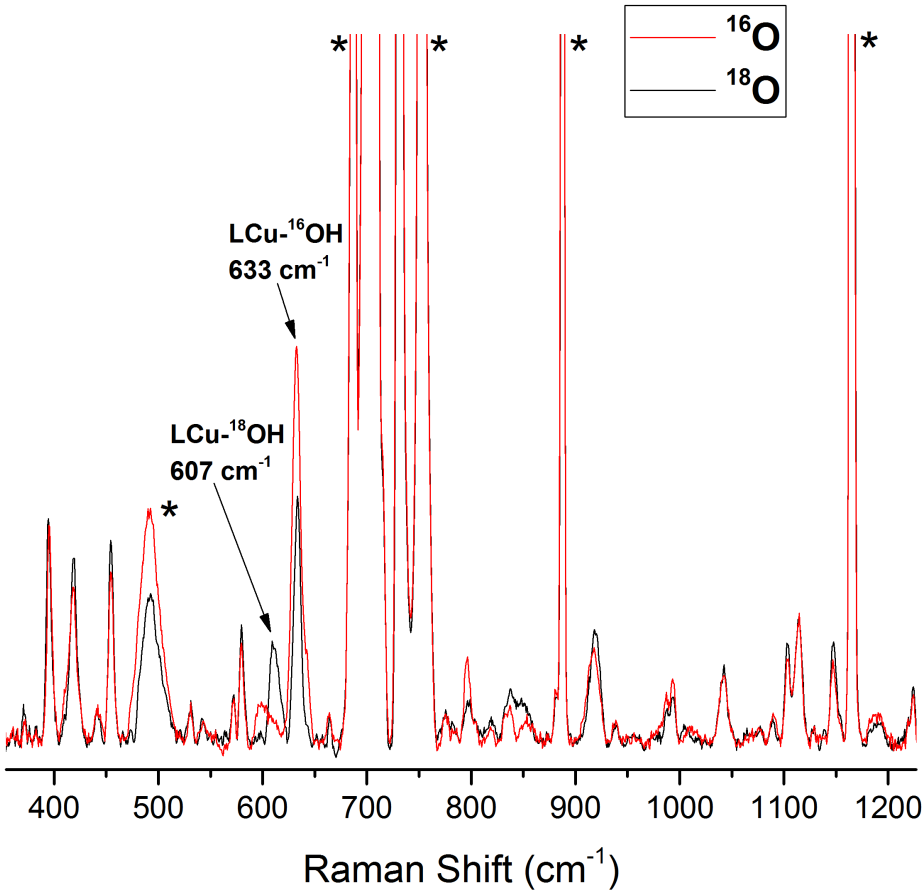


Figure S1. Frozen solution rR spectrum of **1(**^{16}**O)** (red) and **1(**^{18}**O)** (black) in CH_2Cl_2 at 77 K using 515 nm excitation. Asterisk indicates solvent peak.

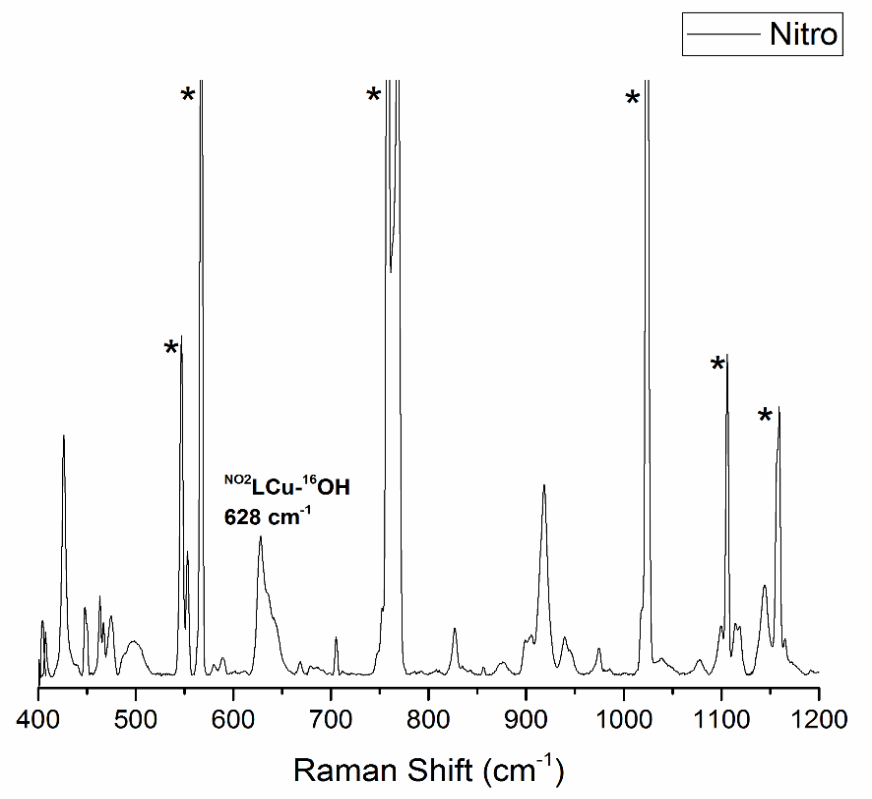


Figure S2. Frozen solution rR spectrum of **2** (black) in DFB at 77 K using 514.5 nm excitation. Asterisk indicates solvent peak.

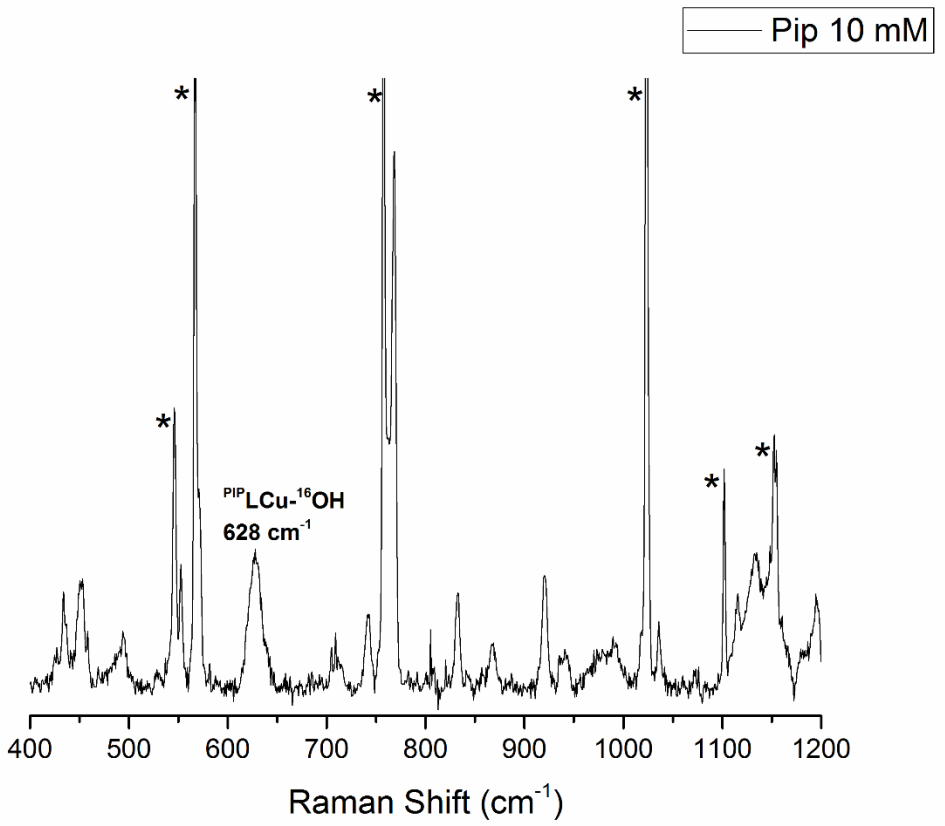


Figure S3. Frozen solution rR spectrum of **3** (black) in DFB at 77 K using 514.5 nm excitation. Asterisk indicates solvent peak.

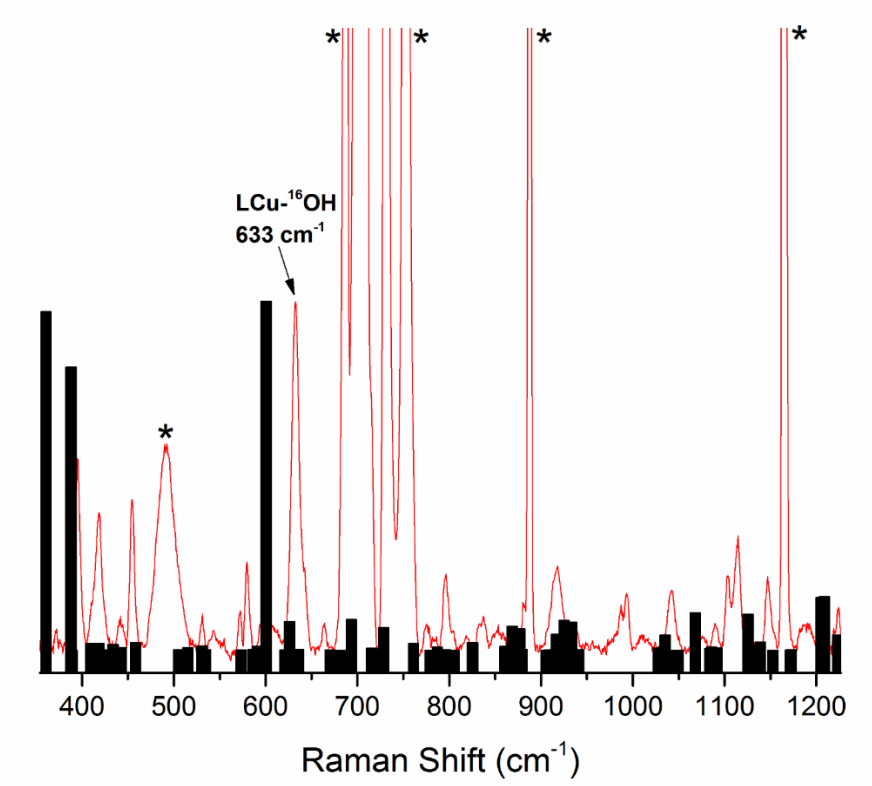


Figure S4. Frozen solution rR spectrum of **1** (red line) in DFB at 77 K using 515 nm excitation. Asterisk indicates solvent peak. DFT predicted rR spectrum (black bars), normalized to the 633 cm^{-1} peak (*m*PWPW/TZVP).

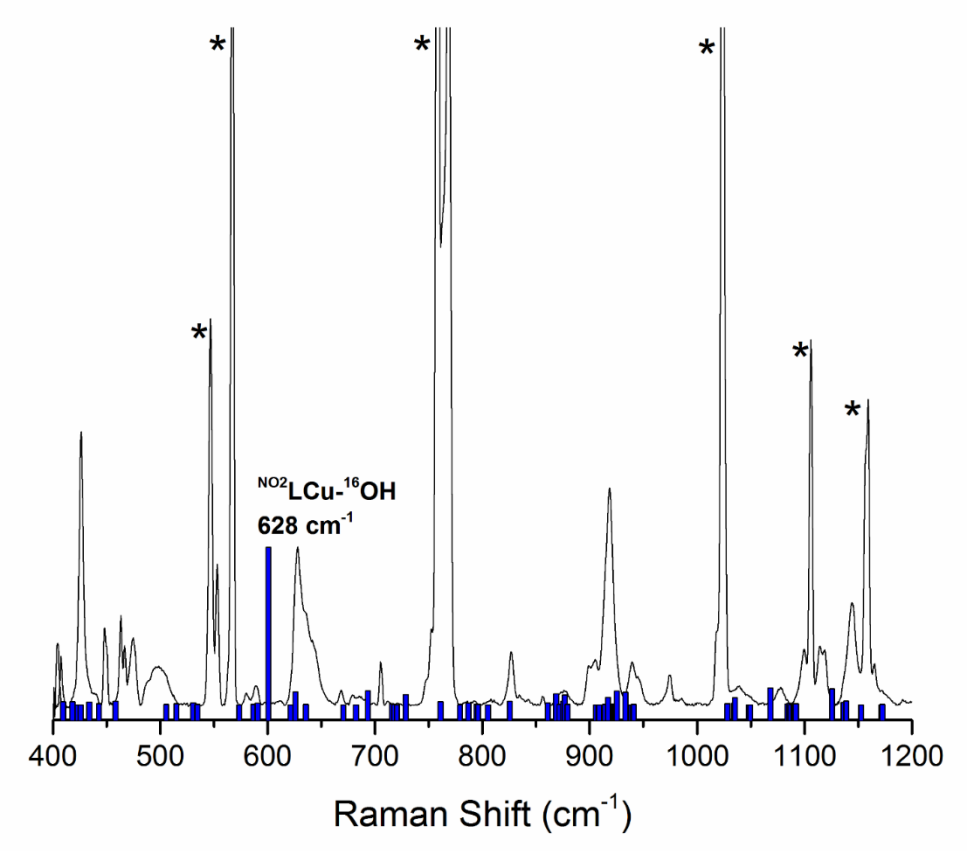


Figure S5. Frozen solution rR spectrum of **2** (black line) in DFB at 77 K using 514.5 nm excitation. Asterisk indicates solvent peak. DFT predicted rR spectrum (blue bars), normalized to the 628 cm^{-1} peak (*m*PWPW/TZVP).

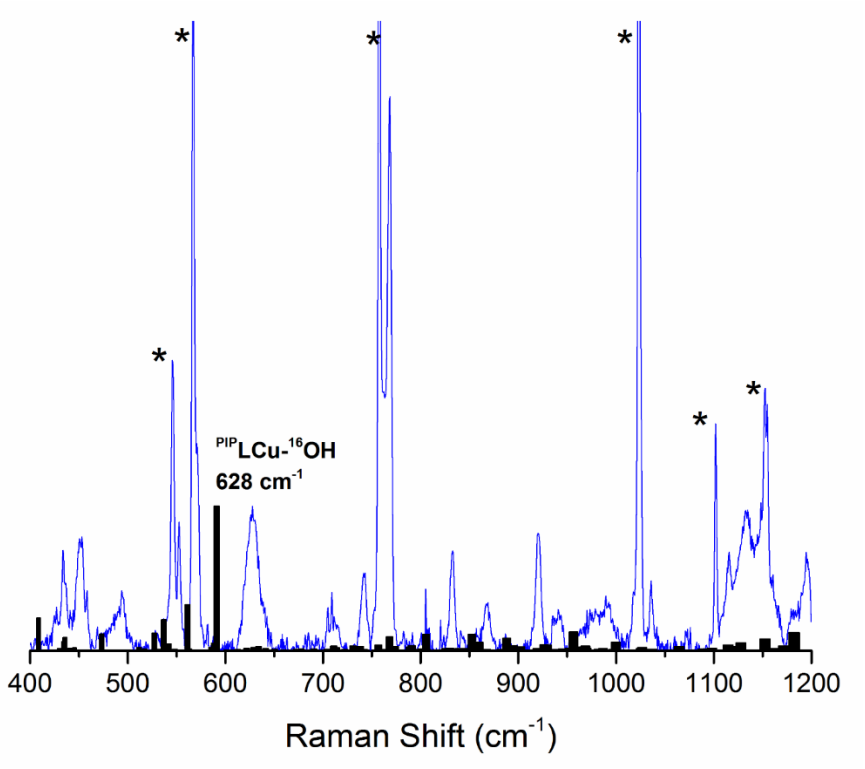


Figure S6. Frozen solution rR spectrum of **3** (blue line) in DFB at 77 K using 514.5 nm excitation. Asterisk indicates solvent peak. DFT predicted rR spectrum (black bars), normalized to the 628 cm^{-1} peak (*m*PWPW/TZVP).

Table S2. Structures mined from the Cambridge Structural Database (CSD)[3], and DFT calculated values using *m*PWPW/TZVP used to construct Figure 3.

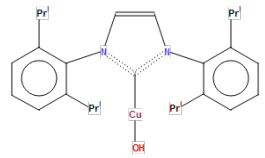
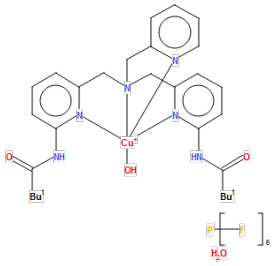
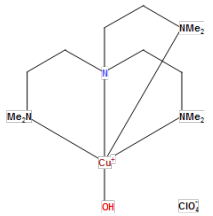
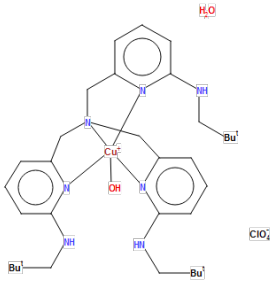
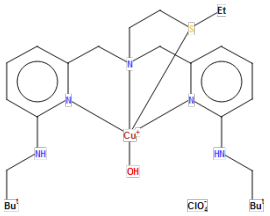
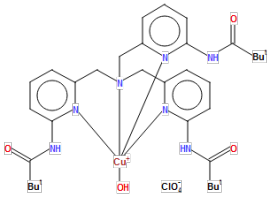
Structure	CSD RefCode	XRD Cu-O (Å)	DFT Calc. Cu-O (Å)	DFT Calc. ν_{Cu-O} (cm^{-1})	Normalized Frequency, ν_{μ} (cm^{-1})
	AKONAQ[4]	1.804(2)	1.805	605	47
	GOWCUQ[5]	1.849(5)	1.925	481	38
	LEFXOJ[6]	1.875(2)	1.878	514	40
	PUXWAG[7]	1.895(4)	1.949	446	35
	UKARON[8]	1.887(1)	1.943	456	36
	YETNIU02[9]	1.878(2)	1.924	457	36

Table S3. DFT Calculated values using *m*PWPW/TZVP used to construct Figure 3.

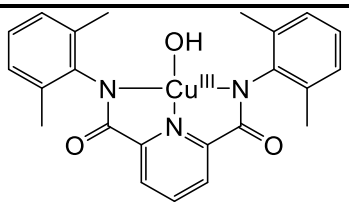
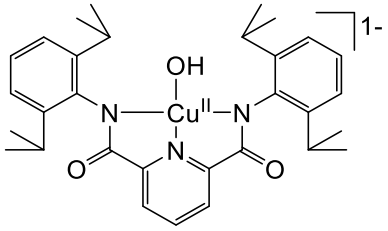
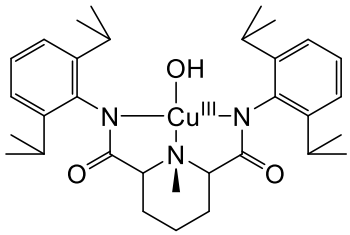
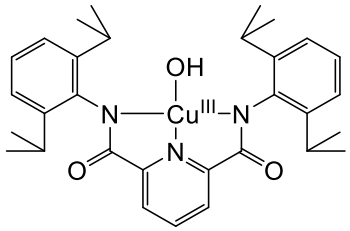
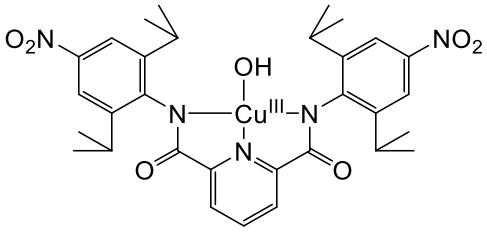
Structure	DFT Calc. Cu-O (Å)	DFT Calc. ν_{Cu-O} (cm^{-1})	Normalized Frequency, ν_{μ} (cm^{-1})
 **^{Me}LCu^{III}-OH**	1.816	601	47
 **[1]$^{-}$**	1.869	516	40
 **3**	1.795	591	46
 **1**	1.815	599	47
 **2**	1.813	598	47

Table S4. Bond distances and frequencies from DFT geometry optimized structures for Fe-O(H) (B3LYP/6-311G) and O-O (*m*PWPW91/DVZP-TZVP) used to construct Figure 3.

Bond Type	Core	DFT Calc. Distance (Å)	DFT Calc. ν (cm^{-1})	Normalized Frequency, ν_μ (cm^{-1})	Ref
Fe-O(H)	Fe-O	1.627	852	69	10
	Fe-O	1.634	836	67	
	Fe-O	1.648	804	65	
	Fe-O	1.648	793	64	
	Fe-O	1.652	792	64	
	Fe-O	1.652	785	63	
	Fe-O	1.669	754	61	
	Fe-OH	1.762	616	50	
	Fe-OH	1.779	601	48	
	Fe-OH	1.812	594	48	
	Fe-OH	1.814	588	47	
	Fe-OH	1.813	565	45	
	Fe-OH	1.850	546	44	
	Fe-OH	1.852	536	43	
	Fe-OH	1.893	494	40	
	Fe-OH	1.905	488	39	
	Fe-OH	1.920	462	37	
	Fe-O	1.671	783	63	
	Fe-O	1.652	792	64	
	Fe-O	1.680	749	60	
	Fe-O	1.817	589	47	
	Fe-O	1.806	610	49	
	Fe-O	1.650	819	66	
	Fe-O	1.770	666	54	
	Fe-OH	1.891	497	40	
	Fe-OH	1.869	526	42	
	Fe-OH	1.884	486	39	
	Fe-OH	1.925	450	36	
	Fe-OH	1.913	477	38	
	Fe-OH	1.936	462	37	
	Fe-OH	1.768	657	53	
	Fe-OH	1.838	579	47	
O-O	O_2^+	1.122	1946	243	11
	O_2 (T)	1.220	1550	194	
	Cu-O_2	1.329	1124	141	
	Cu-O_2	1.322	1111	139	
	Cr-O_2	1.339	1086	136	
	NaO_2	1.369	1087	136	
	Co-O_2	1.380	987	123	

$Cr-O_2$	1.361	1034	129
O_2^-	1.363	1097	137
LiO_2	1.364	1097	137
$Mn-O_2$	1.377	1009	126
NiO_2	1.382	982	123
$Cu-O_2$	1.376	1013	127
$Cu-O_2$	1.358	1041	130
$Pd-O_2$	1.400	941	118
$Mn-O_2$	1.430	937	117
H_2O_2	1.471	892	112
$Al-O_2$	1.691	543	68

Table S5. Bond distances from EXAFS/XRD and experimental frequencies for the data set used to construct Figure 3.

Bond type	Core	EXAFS/XRD (Å)	Exp. ν (cm^{-1})	Normalized Frequency, ν_μ (cm^{-1})	Ref
Cu-O	Cu-(μ-η^1:η^2-O_2)-Fe	1.870	515	40	12
	Cu_2-(μ-O)$_2$	1.810	609	48	13
	Cu-O-O-Cu	1.852	561	44	14
	Cu-OOR	1.887	518	41	15
	Cu_2-(μ-O)$_2$	1.814	610	48	16
	Cu_2-(μ-O)$_2$	1.828	600	47	17
	Cu_2-(μ-O)$_2$	1.806	612	48	18
	Cu-(μ-O)$_2$	1.840	554	43	19
	Cu-OOR	1.810	652	51	20
	Cu-OR	1.8324	592	46	21
Mn-O	Mn-O	1.560	979	79	22
	Mn-O	1.550	975	79	22
	Mn-O	1.771	700	56	23
	Mn-O	1.760	737	59	23
	Mn-O	1.680	746	60	23
	Mn-O	1.555	979	79	24
Fe-O	Fe-O	1.813	671	54	23
	Fe-O	1.680	799	64	23
	Fe-O	1.640	824	66	25
	Fe-O	1.640	839	67	25
	Fe_2-(μ-O)$_2$	1.79	673	54	26
	Fe_2-(μ-O)$_2$	1.78	674	54	27
	Fe-O	1.667	826	66	28
	Fe-O-Fe	1.77	850, 381	49	29
	Fe-O-Fe	1.76	885, 363	50	
	Fe-O-Fe	1.795	838, 409	50	
	Fe-O-Fe	1.77	860, 403	51	
	Fe-O-Fe	1.76	870, 458	53	
	Fe-O-Fe	1.79	827, 395	49	
	Fe-O-Fe	1.78	795, 425	49	
	Fe-O-Fe	1.765	846, 422	51	
	Fe-O-Fe	1.765	850, 425	51	
	Fe-O-Fe	1.79	763, 494	51	
	Fe-O-Fe	1.79	772, 497	51	
	Fe-O-Fe	1.785	770, 499	51	
	Fe-O-Fe	1.80	778, 454	50	
	Fe-O-Fe	1.78	749, 540	52	
	Fe-O-Fe	1.80	745, 537	52	
	Fe-O-Fe	1.785	727, 537	51	

	Fe-O-Fe	1.79	725, 525	50	
	Fe-O-Fe	1.785	749, 528	51	
	Fe-O-Fe	1.765	768, 507	51	
	Fe-O-Fe	1.78	756, 493	50	
Fe-N	Fe-N	1.53	1034	92	30
	Fe-N	1.526	1008	90	31
	Fe-N-Fe	1.54	918	82	32
Mn-N	Mn-N	1.512	1050	94	33
Cr-O	CrO_2Cl_2	1.580	984	80	34
	CrO_4^{2-}	1.660	847	69	
	$Cr_2O_7^{2-}$	1.630	904	74	
	$Cr_3O_{10}^{2-}$	1.598	956	78	
	$Cr_4O_{13}^{2-}$	1.587	963	79	
	K_2CrO_4	1.650	874	71	
	$K_2Cr_2O_7$	1.630	902	74	
	$K_2Cr_3O_{10}$	1.593	945	77	
	$K_2Cr_4O_{10}$	1.587	957	78	
	CrO_3	1.578	975	80	
N-N		1.115	2109	301	35 [a]
		1.113	2031	290	
		1.07	2127	304	
		1.144	2040	291	
		1.08	2116	302	
		1.09	2053	293	
		1.104	2124	303	
		1.11	2038	291	
		1.106	2086	298	
		1.107	2138	305	
		1.107	1979	283	
		1.105	2090	298	
		1.085	2028	290	
		1.12	2004	286	
		1.119	1976	282	
		1.13	2033	290	
		1.106	2041	291	
		1.107	2111	301	
		1.113	2148	307	
		1.095	2153	307	
		1.112	2072	296	
		1.117	1959	280	
		1.136	2043	292	
		1.054	2143	306	
		1.085	1934	276	
		1.099	2142	306	

		1.12	1897	271	
		1.087	2010	287	
		1.102	2090	298	
		1.065	2008	287	
		1.123	2063	295	
		1.094	2122	303	
		1.18	1719	245	
		1.167	1818	260	
		1.237	1414	202	
		1.239	1418	202	
		1.096	2142	306	
		1.235	1548	221	
		1.144	2024	289	
		1.246	1370	196	
		1.286	1270	181	
		1.208	1685	241	
		1.166	1760	251	
		1.2145	1630	233	
		1.239	1503	215	
		1.265	1349	193	
		1.124	2005	286	
		1.132	2007	287	
		1.131	2042	292	
		1.136	1939	277	
		1.151	1770	253	
		1.18	1810	258	
		1.192	1778	254	
		1.215	1625	232	
		1.238	1583	226	
		1.241	1589	227	
		1.12	2164	309	
		1.211	1598	228	
		1.22	1599	228	
		1.185	1696	242	
		1.1	2359	337	
		1.25	1556	222	
		1.45	885	126	
O-O	O_2^+	1.123	1858	232	11
	O_2 (T)	1.208	1549	194	
	O_2 (S)	1.216	1484	186	
	Sm-O_2	1.319	1124	141	
	Cr-O_2	1.325	1104	138	
	Cr-O_2	1.327	1072	134	
	NaO_2	1.33	1094	137	

	$Co-O_2$	1.355	961	120	
	$Cu-O_2$	1.39	961	120	
	$Cu-O_2$	1.392	974	122	
	$Pd-O_2$	1.411	891	111	
	$Co-O_2$	1.429	890	111	
	$Mn-O_2$	1.43	892	112	
	H_2O_2	1.453	880	110	
	$Co-O_2$	1.457	861	108	
		1.302	1123	140	35[a]
		1.347	971	121	
		1.432	920	115	
		1.438	924	116	
		1.424	910	114	
		1.432	931	116	
		1.436	884	111	
		1.428	892	112	
		1.488	868	109	
		1.438	882	110	
		1.46	890	111	
		1.445	873	109	
		1.461	893	112	
		1.44	968	121	
		1.21	1580	198	
		1.33	1098	137	
		1.49	877	110	
S-S	Cu_2-S_2	2.214	442	28	36
	Cu_2-S_2	2.2007	443	28	
	Cu_2-S_2	2.1265	454	28	
	Cu_2-S_2	2.2138	424	26	
	Cu_2-S_2	2.2007	435	27	
	Cu_2-S_2	2.2013	441	28	
	Cu_2-S_2	2.2060	428	27	
	Cu_2-S_2	2.2130	432	27	
	Cu_2-S_2	2.165	440	27	
	Cu_2-S_2	2.1691	443	28	
	Cu_2-S_2	2.073	500	31	
	Cu_2-S_2	2.044	499	31	
	Ir_2-S_2	1.9500	613	38	
	$Mo-S_2$	2.07	528	33	
	$Mo-S_2$	2.01	530	33	
	$Nb-S_2$	2.02	558	35	
	Mo_2-S_2	2.01	540	34	
	$Mo_2-S_2(S_2)_2$	2.08	510	32	
	$Mo_4-(S_2)_5$	2.04	536	33	

Mo_4-$(S_2)_5$	2.05	550	34
Ru_2-S_2	2.01	514	32
Fe_2-S_2	2.02	507	32
Mo_4-$(S_2)_6$	2.08	480	30
Fe_4-$S_2(S_2)_2$	2.04	503	31
Fe_4-$S_2(S_2)_2$	2.05	478	30
Mo_2-$(S_2)_6$	2.04	550	34
Mo_2-$(S_2)_2$	1.98	561	35
Nb_2-S_2	2.03	588	37
Mo_3-$(S_2)_6$	2.02	545	34
Mo_3-$(S_2)_3$	2.03	562	35
Fe_2-S_2	2.01	555	35
Mo_2-S_2	2.04	518	32
Mo_2-S_2	2.00	520	32
S_2	1.892	718	45

[a] Cores not identified by reference 35.

Table S6. Enzyme intermediates with experimental determination of both bond length and stretching frequency used to construct Figure 3.

Enzyme (Intermediate)	Core	Exp. Bond Length (Å)[a]	Exp. ν (cm^{-1})	Normalized Frequency, ν_μ (cm^{-1})	Ref.
HRP-(I)	Fe-O	1.673	790	64	37, 38
HRP-(II)	Fe-O	1.704	789	63	38, 39
CPO-(I)	Fe-O	1.65	790	64	40, 41
CPO-(II)	Fe-O	1.82	565	45	42, 38
TauD-(J)	Fe-O	1.62	821	66	43, 44
Mb-(II)	Fe-O	1.658	805	65	45
sMMO-(Q)	Fe_2-O_2	1.77	690	55	46, 47
oxyHc	O-O	1.51	742	93	48, 49

(a) Determined by EXAFS/XRD and estimated standard deviations indicated in parentheses. Abbreviations: CPO is chloroperoxidase, HRP is horse-radish peroxidase, Mb is myoglobin, oxyHc is oxyhemocyanin, sMMO is soluble methane monooxygenase, TauD is alpha-ketoglutarate-dependent taurine dioxygenase.

Note for Figure S7. The simple correlation we have discovered also seems to break down upon analysis of diatomic molecules in the gas phase (Figure S7). In addition to the well-behaved line already described, four new trend lines (or striations) appear (Figure S7c). Any diatomics featuring –H or $-^2$H bonds form striations above the Badger's rule trend line in Figure

3c (ν_μ < ~300 cm^{-1}), while many metal-metal diatomics fall below the line (ν_μ > ~30 cm^{-1}). It is unclear at this time why these significant deviations are observed for these simple diatomic species in the gas phase, however, our Badger's rule correlation still retains predictive power within the limitations we have outlined.

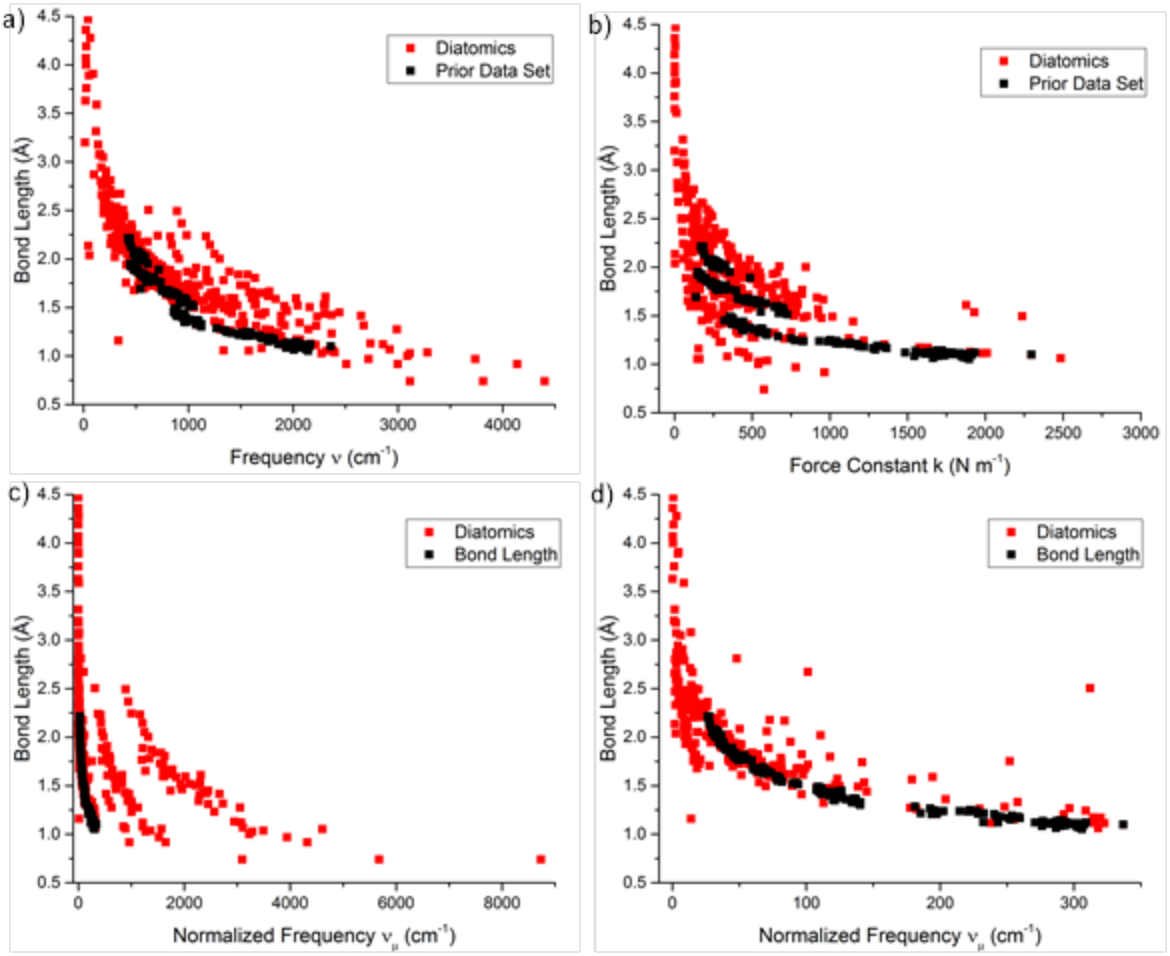


Figure S7. Plots featuring diatomic data[50] (red) with the prior data set (from Figure 3. black) with bond length vs. frequency, ν (a); force constant, *k* (b); and normalized frequency, ν_μ (c). Graph (d) is a zoom-in of graph (c).

DFT Geometry Optimized Structures

Table S7. Cartesian coordinates (Å) for [**1**]$^-$

Atom	X	Y	Z
Cu	-0.03556411473835	0.02447453057463	-0.00008232207279
O	-1.17557718403825	0.27587059441593	1.45945744636751
H	-0.62326362263789	0.49626546187142	2.22948007179556
N	1.13204138775386	-0.29034894785891	-1.53161797885440
C	2.45370567753487	-0.13968637935263	-1.37140464839149
C	3.32069249318627	-0.36957401345754	-2.44086535182861
H	4.39017640034538	-0.24089187733869	-2.28319692270433
C	2.77216060730430	-0.75495470406743	-3.66934702443678
H	3.42657569663352	-0.94064157766068	-4.52238036562030
C	1.38761152483421	-0.90110179757954	-3.80763349645424
H	0.91183247307611	-1.19523978128340	-4.74164300356399
C	0.57981299780818	-0.65716982931229	-2.69505294866769
C	-0.93205806920179	-0.76039726993359	-2.68453979828660
N	-1.43949611087132	-0.47762544292454	-1.46363605081393
C	-2.84042737275677	-0.48388178834145	-1.27213881300093
C	-3.62930042672373	0.61458758436079	-1.70256133175268
C	-5.00945299461565	0.58928812579854	-1.47208567747141
H	-5.62094272440383	1.42957933503369	-1.80730341876371
C	-5.61701101021682	-0.48164460736260	-0.81831610421143
H	-6.69478669892989	-0.48264654015713	-0.64634134408766
C	-4.83300732487496	-1.54867598958252	-0.38328017093314
H	-5.30502305766381	-2.38389706463533	0.13796472463247
C	-3.44979706053423	-1.57063132921497	-0.59548725134600
C	-2.62801388405215	-2.75197979357028	-0.10045732200246
H	-1.58771058469559	-2.55611314176890	-0.39273410190212
C	-2.66160750208567	-2.84968500129292	1.43495191084783
H	-2.30690848828112	-1.90619513483703	1.87182751571673
H	-2.01355057123920	-3.66885659383658	1.78329460173320
H	-3.68043864044971	-3.05070740477847	1.80024609841668
C	-3.05966724015930	-4.06980774392305	-0.76874037236104
H	-3.00367557109192	-3.99466938145361	-1.86297096892710
H	-4.09332452012738	-4.33610002794057	-0.50118336714525
H	-2.40957282464077	-4.89691705963340	-0.44532626690098
C	-3.00687641884899	1.81347476208992	-2.40493341268323
H	-1.92010046167479	1.65940156435011	-2.39849499036727
C	-3.28552560349141	3.12609941826578	-1.65090537997335
H	-2.94396212342878	3.05904274584308	-0.61003727926974
H	-4.35918141337627	3.36547890962423	-1.63985949049221
H	-2.76324454243526	3.96619908676213	-2.13316811317446
C	-3.45522269188349	1.89974156411802	-3.87541667596286
H	-3.21648587813325	0.96691166647587	-4.40115142850019
H	-2.94712161118235	2.73067382168054	-4.38869136290517
H	-4.53973426651909	2.07294490471384	-3.94987213699983
O	-1.53096458867815	-1.07394009875767	-3.73419560322151
C	2.88610243264775	0.28493129296523	0.01716600202575
O	4.09784948730919	0.44723310868167	0.26689496820147
N	1.82240200152625	0.44112961586731	0.83884190642226
C	2.01970416051882	0.82493930330976	2.18475883421234
C	1.75373630327995	2.16459996224066	2.57357670740754
C	1.89867795503842	2.52187028676281	3.91968906878611
H	1.69832508113476	3.55159702873161	4.22198793342164
C	2.29484466995660	1.59071984761579	4.87827699159865
H	2.40517903477574	1.88793256698286	5.92242553427948
C	2.54409407601842	0.27450604411627	4.49144530204329
H	2.84929614348984	-0.45548751050579	5.24369229318629
C	2.40757999802684	-0.13305121136618	3.15914946280984
C	2.68008113133641	-1.58190006879240	2.77907950142728
H	2.40620690731183	-1.69031480588390	1.72161473589516
C	4.17656305667229	-1.92123036190232	2.91023054389491
H	4.77820958856829	-1.23161306947044	2.30534565181861
H	4.37197172417268	-2.94860743381740	2.56716543486305
H	4.50829493414714	-1.84778277377537	3.95715435433682
C	1.80640547292991	-2.56374228878907	3.57966307785418
H	1.97628112133100	-3.59520291125170	3.23677479414215
H	0.74019697391308	-2.33425409640222	3.45473209041038
H	2.03800265749086	-2.52995969119422	4.65445275848397
C	1.34169377481600	3.21329232056992	1.54938501486718
H	1.23782247696183	2.69102221612381	0.58892564758079
C	2.43283290765055	4.28683585648051	1.38070889132244
H	3.39373194354607	3.83010430747228	1.10977254386807
H	2.57946778601868	4.85619447954472	2.31094410695255
H	2.15409907832606	5.00103405975714	0.59136462443265
C	-0.02421569003729	3.83829817456512	1.88137543467897
H	-0.79840531025921	3.06161526606336	1.93672798998838
H	-0.31670209582870	4.55732925929260	1.10172097563640
H	-0.00106184258485	4.37790447188470	2.84009928969222

Table S8. Cartesian coordinates (Å) for **1**

Atom	X	Y	Z
Cu	0.05243399893838	0.05556684315186	-0.15420836659202
O	-1.10773608645592	0.37442792395016	1.20493217392966
H	-0.59432911949861	0.70670248029755	1.96587651365100
N	1.17853098245986	-0.27674827222176	-1.61935500368437
C	2.48520711517521	-0.05321517437184	-1.45974028873672
C	3.35222845778104	-0.27820123175862	-2.52693145254756
H	4.41660275266467	-0.09355776643995	-2.39132063370805
C	2.80918046803375	-0.73435288998520	-3.73497945684745
H	3.46480376949294	-0.91923713569107	-4.58566652200514
C	1.43194233469462	-0.95413560677397	-3.86083195385773
H	0.97284469191333	-1.30729588870979	-4.78266244713633
C	0.62276658575707	-0.70844398852012	-2.75324781189920
C	-0.87567570211106	-0.87367551062645	-2.66399424650217
N	-1.33298748347703	-0.54346519239849	-1.41543871734446
C	-2.69823082092689	-0.60730957684609	-1.07753367031616
C	-3.53155240086787	0.52130640870221	-1.30565702747946
C	-4.88778441393209	0.41657647804913	-0.98721493408356
H	-5.54765673408706	1.26479948900765	-1.17104245225409
C	-5.41160014545189	-0.75227056928844	-0.43623709745745
H	-6.47256500250810	-0.81086872023619	-0.19088828754115
C	-4.57905770994255	-1.84381994307721	-0.19052837738974
H	-4.99950829775840	-2.74822741092220	0.24999945358821
C	-3.21628980848386	-1.79562607155500	-0.49287090242695
C	-2.33596732366619	-3.00821507807684	-0.23924734670380
H	-1.29363007055128	-2.68567641104874	-0.36797502297195
C	-2.47703896660912	-3.54077569866976	1.19630850860292
H	-2.29485608214632	-2.74633208635767	1.93016297561808
H	-1.75472604547134	-4.34977067913413	1.37313957747624
H	-3.47929732639983	-3.95233749669327	1.38014526933531
C	-2.61373638097298	-4.11404243325416	-1.27667541771126
H	-2.48143086406863	-3.74282428407542	-2.30107005122242
H	-3.64393267815093	-4.48670067455980	-1.18383900170759
H	-1.93337407974916	-4.96385829190315	-1.12406384790862
C	-2.99238765658551	1.80703354834134	-1.91128789847031
H	-1.90135702821220	1.70268279452839	-1.98345106152764
C	-3.27882632120297	3.02555462321364	-1.01560137615402
H	-2.88530043126104	2.86973853068202	-0.00357648447022
H	-4.35676842153662	3.22423032855431	-0.93534071229390
H	-2.80897174647956	3.92512301235525	-1.43697643659742
C	-3.53725736119797	2.01732228179207	-3.33752876166125
H	-3.30989533526082	1.15714789671111	-3.98002325829942
H	-3.09318165027757	2.91565411708061	-3.78946120739562
H	-4.62829440967379	2.15273482528903	-3.32471455436712
O	-1.54120635147597	-1.26209366426295	-3.62682567692399
C	2.84858095633635	0.43379129686137	-0.07695166754486
O	4.01389005851469	0.68494797757109	0.23806255890978
N	1.73628651694074	0.53912581827824	0.71726889521624
C	1.83962267261903	0.97241972402025	2.06403828486033
C	1.79984950643355	2.36081211897124	2.36188680444474
C	1.88522961400533	2.75189274807695	3.70253822004046
H	1.86443334019581	3.81344455973937	3.95320675750296
C	2.00052978376018	1.81154131413834	4.72406175596681
H	2.06592745782710	2.13991020469483	5.76179341880155
C	2.02882952801421	0.45137762940595	4.42011045447942
H	2.11791713479552	-0.27591191000636	5.22716472921232
C	1.94414878535292	0.00292341281614	3.09773108331417
C	2.00707456591286	-1.48646836118440	2.79268517749815
H	1.74296907405330	-1.61328924758255	1.73369099225173
C	3.44070371070338	-2.02139437471787	2.97990781650090
H	4.15983311278509	-1.45317284380746	2.37715786967917
H	3.49813739627842	-3.07885515510746	2.68468411397579
H	3.75059695298790	-1.95050783268270	4.03226852904905
C	0.99392226507581	-2.29736009381390	3.61724604272510
H	1.00711027196690	-3.35053156636913	3.30402010052717
H	-0.02545304492748	-1.91436745605959	3.48015883344722
H	1.22705763394973	-2.27042149835598	4.69086839856505
C	1.69493389557067	3.41469433365941	1.26977091584876
H	1.57667064443947	2.88585196725161	0.31467263439903
C	2.98640191254615	4.24999009828886	1.18216261155353
H	3.86157985019334	3.60768350507698	1.02422450994120
H	3.14901928910833	4.82750274642393	2.10353686096631
H	2.92505352777230	4.96403726591277	0.34836684306991
C	0.45780936677044	4.31110104971705	1.45267166877836
H	-0.46258714230172	3.71373233574339	1.49258060323591
H	0.37027953836114	5.01643495981293	0.61395354653441
H	0.51879092349886	4.90153843897864	2.37721599324427

Table S9. Cartesian coordinates (Å) for ^{Me}**LCu^{III}-OH**

Atom	X	Y	Z
Cu	0.00817935040076	-0.06454268629597	0.01620223080041
O	-1.14403437328168	0.15979448039551	1.40145116713953
H	-0.64275980218238	0.49812479502953	2.16767419634998
N	1.11944172387145	-0.28038198372650	-1.48109264357391
C	2.42031377943720	-0.02135537570799	-1.32901029296226
C	3.27681718584408	-0.15975304066222	-2.41914056090415
H	4.33644260498963	0.05296289087848	-2.28850825863576
C	2.72950315239592	-0.56741336035274	-3.64236779555116
H	3.37696616804660	-0.68356726825855	-4.51120476580289
C	1.35726220543300	-0.82035992384245	-3.76111259389468
H	0.89269757302322	-1.12957021028543	-4.69583325253738
C	0.55902455832218	-0.66445058858994	-2.62946062327811
C	-0.93575344956130	-0.85816508590098	-2.53587699662668
N	-1.38118048339079	-0.64444970738028	-1.25719126244470
C	-2.74320473999677	-0.68343800413905	-0.91905730561762
C	-3.59984784372472	0.38120834785126	-1.30106823721273
C	-4.94813018483548	0.30798672795398	-0.94553089535581
H	-5.61964508408472	1.11496243190115	-1.24159584030910
C	-5.44138119072661	-0.77471765415754	-0.21456514730560
H	-6.49675115894451	-0.81163596321117	0.05671395486215
C	-4.58622463336339	-1.80697065154795	0.17274576974769
H	-4.97463165181967	-2.64918367647389	0.74668209080838
C	-3.23006124813326	-1.77890082026119	-0.16058885617773

C	-2.30705893330362	-2.88363510588354	0.26884840905081
H	-1.56723764408257	-2.49930509750571	0.98554159193293
H	-2.86634438343558	-3.69425828378283	0.75073881147943
H	-1.75425359336476	-3.30251631290311	-0.58300511996910
C	-3.07468916644637	1.54906969587906	-2.08755566844004
H	-2.19812647181032	1.99685311840840	-1.59863173359439
H	-2.76575589550559	1.23561961192856	-3.09532981072604
H	-3.84275964582321	2.32421588677930	-2.19241999053067
O	-1.60774314283427	-1.17751057044069	-3.51924364947046
C	2.78816256140028	0.42099860593143	0.06792903683646
O	3.94414444634405	0.72556319636963	0.36965411634738
N	1.69131671378842	0.41926888424007	0.89084162527449
C	1.78728377653346	0.84134421671184	2.23790366969484
C	1.82348819482016	2.22408133325123	2.54416777706084
C	1.88644956343255	2.60489526667230	3.88854715531616
H	1.92092810787852	3.66638272378062	4.13721650985733
C	1.90265805916580	1.65105368605384	4.90681756987921
H	1.94812329380971	1.96786220946158	5.94890360487544
C	1.85876653799778	0.29235548157811	4.59270900895397
H	1.87524756276896	-0.45183685924326	5.38989639869021
C	1.79733401313706	-0.13705836407777	3.26272739196408
C	1.76052759539452	-1.60285814205836	2.92482971978385
H	0.83210439260226	-1.86322067165206	2.39601377346327
H	2.59554450464452	-1.88216291173506	2.26776686506041
H	1.81902745461535	-2.21303960244653	3.83369413496129
C	1.81406514330223	3.25563569180452	1.45001109258153
H	0.97389563391374	3.09917188566205	0.75901641704344
H	1.73278551904470	4.26592668821013	1.86758169478618
H	2.73884502429347	3.20400803597016	0.85752066631930

Table S10. Cartesian coordinates (Å) for **2**

Atom	X	Y	Z
Cu	0.11176989442788	0.02868269097871	-0.17239018786638
O	-1.06926319224760	0.32415370163965	1.17341247551893
H	-0.58150391337219	0.66393193824948	1.94715156655099
N	1.25011848007658	-0.28781465771990	-1.63513629480773
C	2.55478242103506	-0.06230824779193	-1.46451414928116
C	3.43068316350674	-0.27779543359550	-2.52622236267132
H	4.49373509386529	-0.09190488252201	-2.38177190750740
C	2.89776665546602	-0.72707626092475	-3.74153035429905
H	3.56009258427222	-0.90439414803113	-4.58843062112725
C	1.52192788998982	-0.94966477076713	-3.87912309932021
H	1.07105467394663	-1.29777628319299	-4.80696304149349
C	0.70422277791592	-0.71369787356459	-2.77587725340189
C	-0.79408435620819	-0.88347780433458	-2.69616865802487
N	-1.25733651841004	-0.56272453190039	-1.44609966023485
C	-2.62239967134533	-0.62853203092516	-1.11136096700676
C	-3.45447875141417	0.50278214836723	-1.33806142515794
C	-4.80836846213211	0.40567258678172	-1.01711244746701
H	-5.49034739661152	1.23570112132956	-1.18672041300640
C	-5.30532517352415	-0.77162631458463	-0.46891267956084
C	-4.49559494350882	-1.87407592315995	-0.21733782271961
H	-4.94188961607331	-2.76375349387913	0.22114792755507
C	-3.13691264581260	-1.81953100485592	-0.52631279356150
C	-2.26093894837085	-3.03577565447123	-0.27822319562602
H	-1.21767102830633	-2.71257307220539	-0.39667329548605
C	-2.41733957597187	-3.58330962174533	1.14997775770859
H	-2.24032385895210	-2.79895078152553	1.89577464731047
H	-1.69837556337301	-4.39565180886959	1.32240749026174
H	-3.42125571582196	-3.99594388809836	1.31958641113606
C	-2.53641733121284	-4.12797999106636	-1.33120215326570
H	-2.39514734804650	-3.74763850307435	-2.35100983834159
H	-3.56785027447687	-4.49868336218318	-1.24883620602131
H	-1.85979130393931	-4.98070698304387	-1.18163377930299
N	-6.75365475091645	-0.85229287664940	-0.13415792363641
O	-7.17390576463810	-1.91209746857416	0.34491387035182
O	-7.45048049579199	0.14494448503841	-0.35513663952325
C	-2.92183849732798	1.78808596987269	-1.94897509925346
H	-1.83034284608769	1.68810271912105	-2.01873948377641
C	-3.21984197808099	3.00923305110435	-1.06077309859029
H	-2.82794932004116	2.86529767871429	-0.04639337395097
H	-4.29893809574805	3.20201282779729	-0.98519247739457
H	-2.75548109273131	3.90824086839338	-1.48834086927036
C	-3.46893039562024	1.98421416026289	-3.37672223587592
H	-3.23710406019911	1.12239899782329	-4.01530710244357
H	-3.02968994402967	2.88236437739534	-3.83263667383267
H	-4.56029886764384	2.11487378854054	-3.36390133807607
O	-1.45996213121847	-1.26542980257450	-3.65921098847689
C	2.90400635769833	0.41611889995122	-0.07585964531746
O	4.06134736344622	0.66988070052652	0.25880664025384
N	1.78231749642650	0.51325010073540	0.71021004035914
C	1.87916531726636	0.93764556372424	2.05860982662596
C	1.84184379060052	2.32655373458052	2.36177930770173
C	1.92442173727975	2.71603626702159	3.70041223879284
H	1.90770732227363	3.76601634096223	3.98610441442362
C	2.03539852109935	1.75240792652201	4.69586018877330
C	2.06299642736598	0.39170540694371	4.41069955964872
H	2.15085399402333	-0.31523710131230	5.23238865937446
C	1.97942715592716	-0.04122390010673	3.08579285154909
C	2.04008810846613	-1.52937814728564	2.77701079897466
H	1.78183383000344	-1.65105077240605	1.71610603604235
C	3.47207599790022	-2.06619384477313	2.97295165041844
H	4.19773338120940	-1.49924501852913	2.37684871259838
H	3.52734245870171	-3.12242693790265	2.67473195332718
H	3.77449296021863	-2.00066206753533	4.02751494133993
C	1.01995477875028	-2.33622715942730	3.59702956257108
H	1.03372926020060	-3.38902563164582	3.28395181465980
H	0.00159796342980	-1.95241971278502	3.45467464586260
H	1.24760359973352	-2.30987330001143	4.67152912686407
N	2.12577266070420	2.19118173851848	6.11620552814661
O	2.22973840607458	1.31399133340578	6.98084919260368
O	2.09210666361407	3.40575334326730	6.34394546928446
C	1.74148279915084	3.38969492910977	1.27903216199515
H	1.63012895743276	2.86805783752188	0.31937225677442
C	3.03199671302479	4.22829619711227	1.20956170282056
H	3.91143255861829	3.59138145597787	1.05369632996831
H	3.18451517277115	4.80128658804816	2.13512464281513
H	2.97358686456884	4.94695136600852	0.38010492229703
C	0.50098956780480	4.28083869148499	1.46718068232048
H	-0.41929262151505	3.68275021530758	1.49849949301473
H	0.41617506836328	4.99295262201934	0.63452622130485
H	0.55829954207120	4.86358435939220	2.39643221607737

Table S11. Cartesian coordinates (Å) for **3**

Atom	X	Y	Z
C	0.34287174893289	-0.15480732180605	-0.17101575671476
C	-0.40504545060932	-1.15468255064008	-1.05657021048599
N	-0.89200287311753	-0.60333336033794	-2.19488707828081
C	-1.84885209587037	-1.28667208032454	-2.97426267974072
C	-1.46550139689663	-2.27044430640134	-3.90450566461229
C	-2.45790462886265	-2.93470606587074	-4.61700358730645
C	-3.79544754958989	-2.63348527554833	-4.43870572283270
C	-4.16348451355568	-1.65532413865432	-3.53061119299260
C	-3.21136539758352	-0.96536236467985	-2.79345218560232
C	-3.66526885962690	0.06794631937608	-1.78705556126462
C	-4.19211409810886	-0.60647990185965	-0.51813573673587
H	-3.44740548212522	-1.27767206084960	-0.08379205408891
H	-5.08218525738830	-1.20271922664295	-0.73785101673015
H	-4.46840261266361	0.14158352857639	0.23088625759166
C	-4.69035734438179	1.03350300824808	-2.37081088668710
H	-4.94019296151151	1.81066483560034	-1.64275703804439
H	-5.62254609740850	0.52872988626105	-2.63552505035393
H	-4.29614160259166	1.51074826710375	-3.26911878579986
H	-2.79008844286014	0.66131768161876	-1.50974035865111
H	-5.21390310802816	-1.42286165769768	-3.39600964657633
H	-4.55319604907588	-3.16349168969568	-5.00534154371041
H	-2.17669024093347	-3.70660935101880	-5.32522644575618
C	-0.02773617451773	-2.68316144367565	-4.11885370960494
C	0.21545660628447	-4.08001436689988	-3.54286318374341
H	-0.02945704508741	-4.11393730525798	-2.47973671145001
H	1.26164712696238	-4.37167956689534	-3.67830835509222
H	-0.40199460566706	-4.81982515558609	-4.05895799442365
C	0.36123038910727	-2.64130723139252	-5.59464831416408
H	0.20818468740895	-1.64819795108983	-6.02271396614428
H	-0.23256717349468	-3.34932375727109	-6.17678678027981
H	1.41038679644964	-2.92544977087591	-5.72061086578487
Cu	-0.30785337562254	1.16747221444620	-2.56475690442707
N	0.84624831341516	0.96149124157115	-1.01447535473070
C	1.00980001280355	2.30529186694769	-0.39389895832546
C	0.01067767042462	2.62478576180501	0.70847610156007
C	-0.11009708204478	1.48260262889099	1.69681377746188
C	-0.60122805217775	0.25797828347280	0.95222070221683
H	-1.59368766249997	0.46226970299553	0.53751726608212
H	-0.70423654811842	-0.61158794714855	1.60339215351161
H	0.85649406616828	1.28276823297359	2.17539180498689
H	-0.81086477114327	1.74364886943522	2.49311888293812
H	0.35402540861909	3.55015079907541	1.17454399812538
H	-0.97078320139293	2.83843042251562	0.26878984358189
C	0.91066895972407	3.38539047191061	-1.47474811060399
N	0.31505641129037	2.97090326248037	-2.61822465057732
C	0.30643530815610	3.82507012265584	-3.75031576350772
C	-0.90369787736151	4.39786399708157	-4.19470935982233
C	-0.89320025346091	5.15129508541333	-5.36550095017139
C	0.27882549323271	5.37908987219601	-6.06480483849763
C	1.46909201896942	4.86189266965761	-5.58706878200811
C	1.51155762639393	4.08535381895016	-4.43594962638253
C	2.85232253342410	5.38374900794219	-3.94995113828231
C	3.53998960463814	2.69551155787435	-4.98111058897662
H	2.88189570331774	1.89133009357564	-5.32066132722001
H	4.44192011583154	2.24513600954785	-4.55522138088112
H	3.84422825018638	3.26898579016740	-5.86036780008063
C	3.75202069857295	4.73628542747090	-3.50489514158120
H	3.23984133726107	5.35068473352115	-2.76349590085647
H	4.03627274192672	5.36988990370541	-4.34944561240807
H	4.67113498201136	4.34861589126127	-3.05582455251017
H	2.67133313372582	2.97734546510630	-3.06493165409172
H	2.39220096799197	5.07307562153348	-6.11652006472750
H	0.26533707097457	5.97060973917352	-6.97340120674780
H	-1.81803571924553	5.58132410246606	-5.73001779960078
C	-2.16641261082352	4.30968637332730	-3.36507271654298
C	-2.20982029746049	5.50681454589990	-2.41188901803308
H	-3.06495674414854	5.43072475934111	-1.73337976115329
H	-2.31253708270914	6.43578563581955	-2.98064592376662
H	-1.29836140603778	5.57847133031588	-1.81451300076661
C	-3.44463896579761	4.23944031116827	-4.19152471223758

H	-4.30659156115701	4.13653460671759	-3.52846572390127
H	-3.43691285989390	3.38750882139215	-4.87616332945697
H	-3.60192382424942	5.14775215771062	-4.77939788508691
H	-2.10805010605843	3.39904144492080	-2.76552798421263
O	1.31494174196659	4.51101106100571	-1.23867757811866
H	2.01818086151655	2.35698180188733	0.03154278433455
C	2.13546714077085	0.53270053269782	-1.60494380155796
H	2.87976136606791	0.41910873123839	-0.81015569889542
H	2.48225200041546	1.27117332126309	-2.32315541887313
H	2.00454934384745	-0.42230609643418	-2.11387213199627
O	-1.23793720253996	1.19642087703339	-4.09936299448707
H	-1.02526777782519	2.01694811677640	-4.56326565659686
O	-0.59157830636173	-2.29184846822032	-0.66342216194869
H	1.20887486576032	-0.65705966655619	0.27092981278441

Table S12. Cartesian coordinates (Å) for CSD Refcode **AKONA**

Atom	X	Y	Z
C	0.07562370427412	0.34293711124306	0.08570330896645
C	0.01936025173225	0.10691437850531	-1.41780858920227
C	1.17105305501517	0.09903661355314	-2.23188984402227
N	2.45156120744893	0.38581778486146	-1.62547336097130
C	3.28467176572128	-0.56954460613435	-1.08852943014619
Cu	3.03527516073791	-2.40968468256640	-0.98816534948781
O	2.71920488530727	-4.18549557871790	-0.93069642354011
H	3.45278492788972	-4.65970022599381	-0.50720602457747
N	4.36072738644905	0.16225484654354	-0.63840045760506
C	4.19690322060907	1.52182618063718	-0.88894260478986
C	2.99453531684109	1.66241623685921	-1.51055639809200
H	2.48050744804891	2.54062554346156	-1.87801303935460
H	4.94263562079956	2.25240919417146	-0.60498544975329
C	5.51694344975372	-0.40900040366732	0.01402335859296
C	6.61703946694234	-0.80073771074393	-0.77701141209501
C	7.73827470244800	-1.31838912477289	-0.11443283442852
H	8.60333383727055	-1.63458303608560	-0.69739258763233
C	7.76246211774753	-1.44440552123283	1.27237863578338
H	8.64551156947235	-1.84995097211641	1.76692250335837
C	6.65583442243880	-1.06340947646896	2.02721005314955
H	6.67826827069552	-1.18124176298982	3.11064910708959
C	5.50748183293088	-0.53924973022054	1.41840898987657
C	4.29773982664330	-0.17702841326101	2.26941088811076
H	3.53994730406653	0.26182942808772	1.60737181347295
C	4.63826987634938	0.87353616744581	3.34155773696343
H	5.05993802732918	1.78389287864390	2.89459537225640
C	5.36718281044196	0.48857628856112	4.06784186782271
H	3.73402777394069	1.15470045639337	3.89872294361398
C	3.67838517144989	-1.44067205234876	2.89667494885283
H	3.40081485902218	-2.16944892275585	2.12324501816210
H	2.77444686296682	-1.18198320208091	3.46542784565997
H	4.38179687725398	-1.92684439812264	3.58704085236694
C	6.60339244667846	-0.72602948064813	-2.29793885089810
H	5.67572713970611	-0.22393592976647	-2.60238490377296
C	7.77763206624076	0.10195517420988	-2.84936593429394
H	7.78725924710749	1.11718513997734	-2.43043377396496
H	7.70336719592394	0.18487751528087	-3.94239183121855
H	8.74561730741045	-0.36422580817020	-2.61955855699477
C	6.57789358893209	-2.14125897583044	-2.90711909338761
H	6.51273687469241	-2.08575681363338	-4.00268283666727
H	5.71479388915709	-2.71318639666643	-2.54034219060461
H	7.49003633247109	-2.69863958441825	-2.65189935920026
C	1.12132462293891	-0.16639646459971	-3.61609106140159
C	-0.13652322847154	-0.41579812476331	-4.18125135613478
C	-1.29179139884694	-0.40462827187468	-3.40376645109235
C	-1.21118660456157	-0.14963640162579	-2.03709435443672
H	-2.11944259963384	-0.15843236281181	-1.43447938746349
H	-2.25968623191107	-0.60467553832611	-3.86404019963632
H	-0.20870437416023	-0.63089841648875	-5.24738106498354
C	2.36819208705874	-0.22482760262689	-4.48836118926721
H	3.22869326093754	0.04999892590053	-3.86441025272389
C	2.30419151019896	0.78115211549353	-5.65182876188614
H	2.15247032096099	1.80715874016824	-5.29029776673844
H	1.48476078911567	0.54624054163180	-6.34501393433862
H	3.24014550483892	0.75716392543737	-6.22689891563389
C	2.61270519925672	-1.65797720040805	-4.99804634356949
H	2.69782095610041	-2.36681947799635	-4.16411477768168
H	3.54175857241989	-1.70113376941579	-5.58359557416759
H	1.79208300830936	-1.99473166218036	-5.64665119079487
H	1.11515995407642	0.57623146263643	0.35107495443322
C	-0.78838261242999	1.54314278572385	0.51320282959983
H	-0.49926343893346	2.45890171868419	-0.01984837673704
H	-0.67772051430529	1.72642500044847	1.59089875153340
H	-1.85438929382662	1.36410863387716	0.31676090670345
C	-0.31666570855036	-0.93375736191541	0.85384937170839
H	0.32945747195703	-1.77731708101521	0.57758875897548
H	-1.35641884415483	-1.22043459753974	0.64331758328233
H	-0.22658750674162	-0.77044764543632	1.93691369505379

Table S13. Cartesian coordinates (Å) for CSD Refcode **GOWCUQ**

Atom	X	Y	Z
Cu	0.03890344189644	0.13967871772783	0.02305962864071
O	-1.02664643080342	0.21809019348651	1.62385514369917
H	-1.12578967943912	-0.66191099196941	2.02386013540688
N	1.17497579812969	0.18564135317540	-1.70010477382030
C	1.17587193951630	1.60968432883435	-2.12357777747066
C	1.44667312488948	2.51094341940832	-0.94138840114725
N	0.96772624704588	2.06786693363879	0.24563210804713
C	1.16676706534692	2.81290425655343	1.36697607713174
N	0.68872684136460	2.26174113878874	2.54182655988104
C	1.01115688598462	2.67308528815063	3.84735977750972
O	1.72530497111508	3.64147489333685	4.06642491208799
C	0.41236138891345	1.80433316085240	4.97750716781532
C	0.88571596147567	0.34173749015830	4.82134512207822
H	0.50906798434935	-0.25541149307214	5.66275237318561
H	0.51390965312361	-0.11358995419573	3.89402131501524
H	1.98208022033522	0.27539240318453	4.82602766315470
C	-1.12918060528410	1.87151491907686	4.92271017004220
H	-1.54811450957254	1.29935368179478	5.76173749322133
H	-1.48277505136387	2.90701736158251	5.01322130022853
H	-1.53105238073584	1.44878444815291	3.99352903872389
C	0.90483421386254	2.35910284785801	6.32265260402826
H	0.48704634438917	1.75705724848666	7.14029522593295
H	1.99857250287746	2.33048282889030	6.39265116038267
H	0.59250109956224	3.40017845459506	6.46306837334375
H	0.07151118344799	1.43512277883749	2.40558935519369
C	1.82602109565374	4.06200028553002	1.29263001600672
C	2.30149599192345	4.49882527793692	0.06772813741372
C	2.12873178820299	3.71154555841632	-1.07748199454881
H	2.51197052702840	4.02519022549074	-2.04695631950880
H	2.81508460634649	5.45742297510575	0.00209351735722
H	1.96168550500152	4.63590377217570	2.20269376104728
H	0.17876618049832	1.82368516847236	-2.53477194736904
H	1.91027141673446	1.78224937977131	-2.92684821229995
C	0.48153576899421	-0.70335878599699	-2.66360057385112
C	-1.01128116413322	-0.48568339246215	-2.62354312666731
N	-1.52096037249447	-0.13939109571492	-1.41565216288943
C	-2.86622584464475	0.04787171677495	-1.29079585356604
N	-3.30523673431824	0.44782637019980	-0.04390102409341
C	-4.61785029667576	0.82656703473831	0.30308955030077
O	-5.54101510101430	0.78218545014721	-0.49755917660354
C	-4.80057543818391	1.31811187857867	1.75556533845587
C	-4.43049867510379	0.19013160196440	2.74417957714510
H	-3.36657070246012	-0.07349906395287	2.69333679528868
H	-5.02637322645597	-0.71307544375795	2.55682957510722
H	-4.63957301891815	0.52290726767268	3.76966705100944
C	-6.27655563562377	1.69869617181749	1.94995297478918
H	-6.93754390396462	0.84071184585085	1.78061092333279
H	-6.42725794539798	2.05692800787105	2.97673397154916
H	-6.58017296188089	2.49173336095021	1.25687630521555
C	-3.91347007815351	2.56090105504139	1.99357789163609
H	-4.15775470013377	3.36071217688542	1.28174205810733
H	-4.09238352040209	2.94816187605458	3.00552551182031
H	-2.84344319343155	2.33376924242499	1.90797551824707
H	-2.56034454196381	0.47651706359139	0.68420710859204
C	-3.72470834932879	-0.15880199175496	-2.39751296297172
C	-3.18002628598438	-0.51229428143425	-3.61894590897426
C	-1.79543989930137	-0.66991632580824	-3.75219586525362
H	-1.34029075624453	-0.93148964482125	-4.70586166847664
H	-3.83570043541337	-0.66181485345975	-4.47610196451231
H	-4.79047275950188	-0.01343404526451	-2.25901580989696
H	0.70708319266949	-1.73912101586278	-2.36900786479073
H	0.87186625226659	-0.55881874343403	-3.68409784055837
C	2.53005688769929	-0.30848191523556	-1.35873547283810
C	2.45377898604803	-1.47396810905306	-0.39979440134745
N	1.38935724145524	-1.47565354202920	0.43387311004771
C	1.28747233609697	-2.45412907753411	1.35160205241896
C	2.23663461923266	-3.46421863602018	1.48251985104465
C	3.33326249565159	-3.46607232278500	0.61982791017876
C	3.44134122389178	-2.45789434084099	-0.33842761274440
H	4.28219710001291	-2.43245501290169	-1.03069906029480
H	4.09229044028908	-4.24427041102200	0.68879117208026
H	2.11100286079954	-4.23339584519502	2.24211103782433
H	0.41340373192444	-2.42024079933924	2.00130055994090
H	3.06868469780732	0.51692515951251	-0.87070782280655
H	3.09358238447364	-0.57727693462780	-2.26685478140637

Table S14. Cartesian coordinates (Å) for CSD Refcode **LEFXOJ**

Atom	X	Y	Z
Cu	0.00721450556257	-0.01983335883626	-0.00483629296700
O	1.33480742577782	-1.34872553320652	0.00272101638373
H	1.61851817661813	-1.63372027116239	-0.88117633210949
N	1.36276754263036	1.71807724918912	-0.41757704458745
O	0.43715684866880	2.85535474590273	-0.61901659032367
C	-0.75627428059621	2.77564728099624	0.33021041052316
N	-1.45692186395645	1.45973576953755	0.23210893646923
C	-2.21507172851733	1.15443678889503	1.48366156983337
C	-1.30051552047641	0.61440715926122	2.58077882401886
N	-0.51632173535706	-0.54345324860470	2.09819726630424
C	0.70185320632383	-0.77300158441986	2.90559246189944
H	1.32234820242370	-1.50976246554451	2.38389127102205
H	1.26958375999438	0.15845916846517	2.99680607999272
H	0.44872601372539	-1.13644375590122	3.91617039206293
C	-1.31287342346467	-1.78905987126152	2.08720821473201
H	-0.71644894681335	-2.57676764925895	1.61529232696639
H	-1.57853476926419	-2.09791680835750	3.11350311932594
H	-2.23941077904119	-1.65429552858006	1.51752940031028
H	-0.59065273016759	1.38831466336859	2.90089195632492
H	-1.90746804073571	0.35854069703275	3.46796458846948

H	-2.74873285813032	2.05127719383235	1.84000886140091
H	-2.97960480791973	0.40846025280165	1.23632958843013
C	-2.34849230950175	1.40844229936825	-0.96470527164442
C	-2.58091431676164	-0.02516320563439	-1.43104926506179
N	-1.30176738080579	-0.72343105489033	-1.70812726650776
C	-1.48948666547643	-2.19182418159533	-1.69451876764154
H	-0.51731101777333	-2.68112336224075	-1.81090085846735
H	-1.91290449769005	-2.50443619449607	-0.73535123778116
H	-2.15958519414380	-2.51870761671157	-2.50822591846679
C	-0.75507245391967	-0.32690630572415	-3.02388342688490
H	0.22040100120845	-0.80294609858004	-3.17085477421898
H	-0.62188358316243	0.75895817494165	-3.07749606461603
H	-1.42558122382948	-0.63757391075747	-3.84441041502387
H	-3.23787341828317	-0.01894278499023	-2.31965699185519
H	-3.10897637205896	-0.59544755465746	-0.65561336463404
H	-1.87326895679625	1.98972816837721	-1.76367964030978
H	-3.31380904935269	1.89631748288573	-0.74938687735929
H	-0.41703986332010	2.89718316242186	1.36558877505349
H	-1.45705929789426	3.60260232429196	0.12667529625203
H	0.94627410704852	3.82651135980941	-0.48092317858034
H	0.09681859834344	2.82760826429597	-1.66290391401185
C	2.23953510110546	1.51669198990485	-1.58996375656604
H	2.84202687412779	0.61717152750019	-1.42426747094747
H	2.91468153629539	2.37662922333691	-1.74145950207348
H	1.63595368869023	1.37984788530981	-2.49338330153309
C	2.21505348867027	1.90208631185585	0.77771355759208
H	2.77648880104240	0.97774008502325	0.94960149777824
H	2.91847313142393	2.74147437496594	0.63759479390889
H	1.60117507552919	2.10777874184005	1.66132731911828

Table S15. Cartesian coordinates (Å) for CSD Refcode **PUXWAG**

Atom	X	Y	Z
Cu	0.23936846518072	0.20759523255663	0.45602201982434
O	1.43659619420349	-0.80252656972302	1.61518378371441
H	2.22441080046308	-0.29464488840063	1.87324596594255
N	-1.00922994004021	1.25818397116959	-0.81088087256295
C	-1.14909848803998	0.43916739947278	-2.04169563075596
C	-1.33749262508517	-1.02302053468766	-1.70222230564373
N	-0.65820905182477	-1.45357573463147	-0.61505574776892
C	-0.71309080969015	-2.77484859048325	-0.26979686568742
N	-0.03749157753559	-3.15755400363649	0.83853840805665
C	0.01206063096871	-4.53531945472319	1.31975604323053
C	0.52812516657101	-4.67520417106807	2.77040277101634
C	1.97612247247525	-4.16413921444636	2.89013083702010
H	2.64004911561519	-4.69328875825772	2.19154396430066
H	2.05433765456192	-3.08647448735816	2.68916767478602
H	2.35603976025327	-4.33886908393254	3.90610448917867
C	0.49459548215242	-6.17713647333709	3.11112084393937
H	-0.52430533690353	-6.58311980133535	3.03866863727053
H	1.14137584050426	-6.75669594453612	2.43735052278988
H	0.84758362703589	-6.34413312543620	4.13727888947026
C	-0.39035122027211	-3.91130543622787	3.74087498305337
H	-0.04453508316695	-4.04058763708827	4.77552617061101
H	-0.41010723140260	-2.83565924478291	3.52183094005276
H	-1.42255862242347	-4.28500931591561	3.68529640343430
H	-1.00421853741808	-4.95626140449838	1.28114449770978
H	0.64544694565183	-5.15140434147396	0.65580138321859
H	0.59350406930491	-2.46038978536367	1.25344853432943
C	-1.46363606444147	-3.68634993801557	-1.06556047779980
C	-2.16140529227744	-3.21677321731649	-2.16064558846245
C	-2.11453973391191	-1.85418651494572	-2.49660073554519
H	-2.65687526392124	-1.46027413651401	-3.35370499388198
H	-2.74401530365918	-3.90978829278450	-2.76713747189173
H	-1.48127383040252	-4.74298216899484	-0.81406592965495
H	-1.98059610047105	0.80916821245017	-2.66282925162534
H	-0.22316095678457	0.55828329141344	-2.62123029163126
C	-2.30637366814772	1.44129754647778	-0.11965645048255
C	-2.11345030898302	1.71387497586144	1.35022200020878
N	-1.06591073848731	1.06948650167499	1.91919925232188
C	-0.88871586574128	1.14837509794759	3.27630441806711
N	0.13555829225848	0.43371390478205	3.79002814092383
C	0.47660694766652	0.27398539039372	5.19778987431925
C	1.68318632972900	1.11191663006353	5.70682985196272
C	1.92579992437300	0.70714657038511	7.17203445222543
H	2.16253430251316	-0.36283971987124	7.26048645818134
H	2.76789082688702	1.27122642964358	7.59426595065460
H	1.04341516408321	0.91139314363859	7.79526931255793
C	1.37910600212168	2.61704048800512	5.62936000471335
H	2.24231651310227	3.20075947497954	5.97706206837366
H	1.15801365225415	2.93334882691324	4.60072751638282
H	0.52349738213126	2.88715899836762	6.26442660968105
C	2.93487686447659	0.79501941744586	4.87042580954227
H	3.16455607967888	-0.28051039794443	4.88084654154331
H	2.80466769525138	1.11524180366317	3.82655781864908
H	3.80917036797497	1.32704835569528	5.26865798498602
H	-0.40425483740673	0.48831523697803	5.81829866083422
H	0.70925968701426	-0.79068596718182	5.35143235433643
H	0.63446327529006	-0.15351621171742	3.09649975812367
C	-1.77351299962440	1.94161959854413	4.05961632817874
C	-2.81396467171163	2.60987272205692	3.44969754530068
C	-3.00499319334447	2.50023576603504	2.06212216056999
H	-3.82441800707923	3.00788434681679	1.55779948636070
H	-3.48819690251535	3.22150910475995	4.04860578647456
H	-1.61997757223807	2.02545704868169	5.13128444988550
H	-2.89782242340439	2.23737618903646	-0.60003451409000
H	-2.86472921308004	0.50011691004301	-0.23208359145450
C	-0.30323041573250	2.54261419994718	-1.04214332391344
C	1.15212080499283	2.29182425195200	-1.35835916154869
N	1.67476151371148	1.18273826106302	-0.78190251475112
C	2.96751638731148	0.82597449277847	-1.04860651889917
N	3.38815770213843	-0.35282202369320	-0.52914106115021
H	2.69177940051581	-0.84431766648869	0.04319020387215
C	3.78222858701510	1.67828323358135	-1.84216600116015
C	3.23866735813770	2.82399333481736	-2.38738707389773
C	1.88680409909853	3.13940163668925	-2.17179761796779
H	1.42659352382042	4.01389715201652	-2.62676030847163
H	3.85896481612149	3.47262085800309	-3.00526143627272
H	4.81621114379079	1.41320055471866	-2.04193317667399
H	-0.78578593771997	3.12005448278914	-1.84786840402787
H	-0.39078495879857	3.12940953312256	-0.11536175337315
C	4.72785074895323	-0.92574507209808	-0.60811166949779
C	4.90773262703912	-2.08669968582599	-1.62512651471592
C	4.63879549345082	-1.60369170721147	-3.05970417616678
H	3.61742567866546	-1.21452445746035	-3.16999555704160
H	5.34333610812845	-0.81448003112511	-3.35827497552197
H	4.75528019408865	-2.43296050760660	-3.77046262960232
C	3.95193216673899	-3.24112092443878	-1.27739289357277
H	2.90019427480584	-2.93796552213287	-1.37281094378063
H	4.11364465895389	-4.08898425500017	-1.95642184078687
H	4.11547306100402	-3.59993651799501	-0.25084203070709
C	6.36461315897833	-2.56828410200203	-1.50314580869775
H	6.55496308682837	-3.39655021421087	-2.19823415468068
H	7.07564966033604	-1.76425405028116	-1.74156008588935
H	6.58644378392344	-2.92735892490452	-0.48797000593981
H	5.45010820395206	-0.12890399816519	-0.82812986356304
H	4.98152900943802	-1.30315635016133	0.39459368603009

Table S16. Cartesian coordinates (Å) for CSD Refcode **UKARON**

Atom	X	Y	Z
Cu	0.03265785837909	0.00648310657152	-0.05390672376131
S	1.20244776319695	-1.23308902489908	-1.84934797311315
C	2.31678843541113	-2.38430023674110	-0.91358203292444
C	3.25516445205167	-3.17858903293085	-1.81127933299171
H	3.84866053600507	-3.86924063005519	-1.19632734296850
H	2.70091987742090	-3.77052350706414	-2.54907942120658
H	3.96202910617939	-2.53418770146838	-2.34937519687396
H	1.61226393243281	-3.03809992175648	-0.38503490965026
H	2.85090111719090	-1.80394651763289	-0.15182385685972
C	2.34069155343749	0.15261872557382	-2.27995780432903
C	2.60826972078559	1.08143033320487	-1.10300029469419
N	1.36717353251374	1.56802580240128	-0.44269212356758
C	1.67547180021872	2.12882896081191	0.90412466839269
C	1.94586007917532	1.03299847920164	1.90567759829530
N	1.15022738342134	-0.05568032826182	1.78058231103132
C	1.24064505107964	-1.06929873033373	2.69942460224604
N	0.40415367237564	-2.11499145868648	2.52706774225047
C	0.34950836519569	-3.33150618030967	3.32832443574563
C	-0.82310378284313	-3.42480687503060	4.34503271854406
C	-2.16702388087503	-3.34478182931530	3.60019233906069
H	-3.00242303703074	-3.44875779354386	4.30565620260019
H	-2.25741645766201	-4.14802601033398	2.85455129205759
H	-2.28290516906114	-2.38393129481778	3.08097507546235
C	-0.73632408069528	-2.29753818803979	5.38657500861344
H	-1.57452547106927	-2.36579430886828	6.09314857431308
H	-0.78039739474396	-1.30635355770883	4.91530140927344
H	0.19188916848929	-2.36019583232616	5.97219968586911
C	-0.70299965669533	-4.78988361670816	5.04625049975621
H	-0.76397393644740	-5.61878076699907	4.32651377938116
H	0.24846957514484	-4.88091480593891	5.58984450210265
H	-1.51456948946017	-4.92144328254046	5.77393371456792
H	1.30271282742568	-3.46682438762012	3.85627670792933
H	0.26050022476613	-4.17854997694668	2.62981390096151
H	-0.25750757866661	-2.02519758523955	1.72878858482180
C	2.19245220837908	-0.97434109137578	3.75599469220458
C	3.00920699963170	0.13307730734306	3.84341442578426
C	2.89638241489390	1.17379680007279	2.90391474494738
H	3.52085443262974	2.06280129511493	2.96097502222532
H	3.73835209380879	0.20267340883056	4.65025965581055
H	2.26320881083762	-1.76539689805230	4.49656242517612
H	2.52157787069680	2.83202732005345	0.84533490934559
H	0.79028697062368	2.69788282894978	1.22349310577957
C	0.62240176946257	2.55090113839633	-1.27304082605404
C	-0.79569216909177	2.70587104502622	-0.78164512820158
N	-1.37246677911365	1.56308081531443	-0.33495310034920
C	-2.68566148310029	1.58218226953678	0.06772577393972
N	-3.20347431735088	0.41808383634191	0.50409872024737
C	-4.53244460237828	0.20728079607717	1.06476276505393
C	-5.56946118480584	-0.46125978070938	0.11901571602505
C	-5.04543220512225	-1.82936092428320	-0.35113551395703
H	-4.13575461193042	-1.72300423755914	-0.95827616676363
H	-4.81524625847981	-2.48422520343182	0.50158126142185
H	-5.79783988647827	-2.33675694250871	-0.96957378483124
C	-6.86063536144303	-0.65624810431067	0.93414082147717
H	-7.25943238347180	0.30422741720393	1.29099887253479
H	-6.69072507711678	-1.29931519121862	1.80950159688996
H	-7.63693758085433	-1.12977849266491	0.31878362529290

C	-5.85715404265620	0.43096582468041	-1.09953962225564
H	-6.28807080618034	1.39641008721292	-0.79838137645746
H	-6.58014381153136	-0.05590503650131	-1.76798095548170
H	-4.94730097469878	0.62627850391692	-1.68341219669277
H	-4.93325970320164	1.16059785648986	1.43452913027035
H	-4.40905576846449	-0.43846703005509	1.94772508038061
H	-2.54548873128551	-0.39061697965095	0.49180008805515
C	-3.41707900259293	2.80491030808604	0.00827762561700
C	-2.79944374725389	3.95442970667081	-0.43207253571004
C	-1.45284537523516	3.92267937992739	-0.83874767872278
H	-0.94365849893231	4.81597426594982	-1.19389351443956
H	-3.35948382529786	4.88841280306208	-0.46880808344874
H	-4.46156538015036	2.82281981198675	0.30428404550250
H	0.59999206931660	2.17165003789556	-2.30401067347693
H	1.14321467022853	3.52197285972043	-1.28940260623070
H	3.18979537924474	0.55507801386114	-0.33561892219650
H	3.21496408406991	1.94157893033602	-1.43879442137857
H	3.28267510073957	-0.26214496821019	-2.65809124689478
H	1.85942062185782	0.66429064704577	-3.12193642780526
O	-1.17942238839704	-1.45884770768108	0.34597132558953
H	-1.32284563685273	-2.01941875253787	-0.43467897035865

Table S17. Cartesian coordinates (Å) for CSD Refcode **YETNIU02**

Atom	X	Y	Z
Cu	-0.18039750050401	-0.13204961883325	-0.04565434142594
O	-1.01754425856161	-1.45934779957418	-1.15846013151590
H	-1.98019937179107	-1.34238347723805	-1.22403441317873
N	0.82667709717894	1.19433645980383	1.15021755471634
C	0.84503226240239	2.48563556948678	0.41944832939845
C	1.15706118943619	2.27110572077288	-1.04414665368548
C	1.81399692187291	3.23589338491543	-1.79445152915901
C	2.02373694222846	2.97619940021459	-3.15385302694097
C	1.61254103055567	1.77481444612933	-3.70659675569160
C	0.98460946976076	0.81683033669450	-2.87679552525241
N	0.73787940662698	1.09305286853247	-1.56620279662719
N	0.59416546823460	-0.43936767300677	-3.30753716785857
C	0.97365574955999	-1.06020740713162	-4.51571752976053
O	1.60284282863812	-0.46479906052659	-5.37836600916641
C	0.56285200227815	-2.54217825619230	-4.65686453964877
C	1.20399078886466	-3.36679172731550	-3.51769779024209
H	0.97053157726456	-4.42984322813816	-3.66389863310244
H	0.82678054842203	-3.07679950845264	-2.52913036559602
H	2.29706785896920	-3.26085954200989	-3.52032816405200
C	-0.97507250759493	-2.67002138751418	-4.61070652375000
H	-1.44586470215120	-2.06925520257565	-5.40021483085827
H	-1.38734718981917	-2.36334491835558	-3.64143607426155
H	-1.25667558699258	-3.71880065116043	-4.77456218300475
C	1.07661851781841	-3.05424288666839	-6.01146094459052
H	2.16742914128545	-2.97380355731560	-6.08307164313426
H	0.64776412842697	-2.48472998545741	-6.84419701264497
H	0.79676827388627	-4.10912385289126	-6.13053765508446
H	0.03045934879943	-0.97535197050938	-2.61944331855771
H	1.78095414440994	1.53171738825686	-4.74983462831418
H	2.51856172798626	3.71468673382614	-3.78379603507235
H	2.15182813973026	4.16225645270551	-1.33305152515694
H	1.56793108937441	3.18193287572421	0.87423111512859
H	-0.15404679309266	2.93122822823502	0.52212057892773
C	2.18279875658642	0.61864233838658	1.33059237212021
C	2.08730153725351	-0.85623516401276	1.63745586407858
C	3.02283403805223	-1.49875030105749	2.43486788547070
C	2.87204592590092	-2.87524090200956	2.64245515327836
C	1.80246487506416	-3.55059965684378	2.08038403825422
C	0.86860751032794	-2.83189988208370	1.29832964301556
N	1.03435367114588	-1.49811154689887	1.07452861764209
N	-0.24681859579196	-3.40084252679440	0.71572963994647
C	-0.80302885586051	-4.65510587471956	1.02636910513925
O	-0.28762207806399	-5.41142976586508	1.83742154603307
C	-2.11877989341268	-4.99074145532883	0.28861656159268
C	-1.88356149277223	-4.98773872508587	-1.23707385248110
H	-1.10812760210924	-5.71289790571871	-1.51745904776240
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H	-2.81215857839421	-5.27643417077309	-1.74806454663315
C	-2.57697548970998	-6.38818604534279	0.73370711143050
H	-1.82699642174847	-7.15017864579794	0.49192020877088
H	-3.51261635767873	-6.64552970936674	0.22010762585852
H	-2.75108917269802	-6.42763788371143	1.81516907404816
C	-3.20174393959449	-3.95515221484703	0.66765541304005
H	-4.15050669980600	-4.22408994809503	0.18425845215138
H	-2.93936798356912	-2.93834522560638	0.34692327552581
H	-3.37118885057036	-3.93808588127230	1.75247981149092
H	-0.70792352628029	-2.79057476812536	0.00734132013905
H	1.64304192880745	-4.61180837230542	2.23687596887274
H	3.59328197039590	-3.42121092972221	3.24964205638050
H	3.84441608471743	-0.94179056646082	2.88183112110505
H	2.73447293998373	1.15062818547951	2.12237372664536
H	2.72755508996386	0.76931723033291	0.38738916721542
C	0.06730166925754	1.25888283820256	2.42067286892676
C	-1.42409565945409	1.30864278585025	2.17073072335623
C	-2.30792966329616	1.71571841691343	3.16298061799160
C	-3.67568973617912	1.68094481407443	2.87851990087155
C	-4.11789311800224	1.31532381864241	1.61469891112090
C	-3.15829110069601	0.97756927239733	0.64176078954822
N	-1.83612738797408	0.91324079188668	0.94396940449166
N	-3.46537515926149	0.73991078877920	-0.69578770237770
C	-4.73706983622891	0.78652715617748	-1.30801082945792
O	-5.76082484645777	0.80774585263984	-0.64570806010021
C	-4.71768538812532	0.86079232666847	-2.85003906215430
C	-4.25162865461924	2.28300508869232	-3.24689724198062
H	-3.22062702835066	2.48803076816576	-2.92565716286432
H	-4.90675259240024	3.04992304531423	-2.81424629956406
H	-4.28574666622261	2.38652823137073	-4.33941117816461
C	-3.77376782373593	-0.19191809460904	-3.46390940502841
H	-3.86010821677056	-0.16095180377876	-4.55771411554180
H	-4.03798411897370	-1.20801770991016	-3.14123602074950
H	-2.71306371624623	-0.01424051686827	-3.23335411239247
C	-6.14884530277108	0.62512754360482	-3.35853560329884
H	-6.51055978068552	-0.37342933880192	-3.08394046112236
H	-6.16665277767382	0.71069230622214	-4.45257450115319
H	-6.84675357498765	1.35765778241122	-2.93933335972283
H	-2.65442882866775	0.72596903192700	-1.31141232218811
H	-5.16958930035707	1.30427477920103	1.34918784176985
H	-4.40228379713348	1.96277748961214	3.63970259931545
H	-1.93858832391207	2.03896313411430	4.13486344826663
H	0.38665666901520	2.12417264292949	3.02512294544536
H	0.31140773887570	0.35352551487658	2.99415760849532

References

(1) McLachlan, G. J.; Do, K.-A.; Ambroise, C., Discriminant Analysis. In *Analyzing Microarray Gene Expression Data*, John Wiley & Sons, Inc., Hoboken, New Jersey: 2005; pp 185-220.

(2) (a) Brown, I. D.; Altermatt, D. *Acta Cryst.* **1985,** *B41*, 244-247. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993,** *32*, 4102-4105. (c) Shields, G. P.; Raithby, P. R.; Allen, F. H.; Motherwell, W. D. S. *Acta Cryst.* **2000,** *B56*, 455-465. (d) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Wang, X.; Young, V. G.; Cramer, C. J.; Que, L.; Tolman, W. B. *J. Am. Chem. Soc.* **1996,** *118*, 11555-11574.

(3) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. *Acta Cryst.* **2016,** *B72*, 171-179.

(4) Fortman, G. C.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2010,** *29*, 3966-3972.

(5) Harata, M.; Hasegawa, K.; Jitsukawa, K.; Masuda, H.; Einaga, H. *Bull. Chem. Soc. Jpn.* **1998,** *71*, 1031-1038.

(6) Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1993,** *115*, 11789-11798.

(7) Jitsukawa, K.; Harata, M.; Arii, H.; Sakurai, H.; Masuda, H. *Inorg. Chim. Acta* **2001,** *324*, 108-116.

(8) Tubbs, K. J.; Fuller, A. L.; Bennett, B.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2003,** *42*, 4790-4791.

(9) Berreau, L. M.; Mahapatra, S.; Halfen, J. A.; Young, V. G.; Tolman, W. B. *Inorg. Chem.* **1996,** *35*, 6339-6342.

(10) Green, M. T. *J. Am. Chem. Soc.* **2006,** *128*, 1902-1906.

(11) Cramer, C. J.; Tolman, W. B. *Acc. Chem. Res.* **2007,** *40*, 601-608.

(12) Hematian, S.; Garcia-Bosch, I.; Karlin, K. D. *Acc. Chem. Res.* **2015,** *48*, 2462-2474.

(13) Mahadevan, V.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. P. *J. Am. Chem. Soc.* **1999,** *121*, 5583-5584.

(14) (a) Baldwin, M. J.; Ross, P. K.; Pate, J. E.; Tyeklar, Z.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1991,** *113*, 8671-8679. (b) Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988,** *110*, 3690-3692.

(15) Mizuno, M.; Honda, K.; Cho, J.; Furutachi, H.; Tosha, T.; Matsumoto, T.; Fujinami, S.; Kitagawa, T.; Suzuki, M. *Angew. Chem. Int. Ed.* **2006,** *45*, 6911-6914.

(16) Mahadevan, V.; Hou, Z.; Cole, A. P.; Root, D. E.; Lal, T. K.; Solomon, E. I.; Stack, T. D. P. *J. Am. Chem. Soc.* **1997,** *119*, 11996-11997.

(17) Mahapatra, S.; Young, V. G.; Kaderli, S.; Zuberbühler, A. D.; Tolman, W. B. *Angew. Chem. Int. Ed.* **1997,** *36*, 130-133.

(18) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Wang, X.; Young, V. G.; Cramer, C. J.; Que, L.; Tolman, W. B. *J. Am. Chem. Soc.* **1996,** *118*, 11555-11574.

(19) Chen, P.; Root, D. E.; Campochiaro, C.; Fujisawa, K.; Solomon, E. I. *J. Am. Chem. Soc.* **2003,** *125*, 466-474.

(20) Chen, P.; Fujisawa, K.; Solomon, E. I. *J. Am. Chem. Soc.* **2000,** *122*, 10177-10193.

(21) Hayes, E. C.; Porter, T. R.; Barrows, C. J.; Kaminsky, W.; Mayer, J. M.; Stoll, S. *J. Am. Chem. Soc.* **2016,** *138*, 4132-4145.

(22) Kerber, W. D.; Goldberg, D. P. *J. Inorg. Biochem.* **2006,** *100*, 838-857.

(23) Cook, S. A.; Borovik, A. S. *Acc. Chem. Res.* **2015,** *48*, 2407-2414.

(24) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990,** *112*, 899-901.

(25) England, J.; Prakash, J.; Cranswick, M. A.; Mandal, D.; Guo, Y.; Münck, E.; Shaik, S.; Que, L. *Inorg. Chem.* **2015,** *54*, 7828-7839.

(26) Costas, M.; Rohde, J.-U.; Stubna, A.; Ho, R. Y. N.; Quaroni, L.; Münck, E.; Que, L. *J. Am. Chem. Soc.* **2001,** *123*, 12931-12932.

(27) Xue, G.; Wang, D.; De Hont, R.; Fiedler, A. T.; Shan, X.; Münck, E.; Que, L. *Proc. Natl. Acad. Sci. USA* **2007,** *104*, 20713-20718.

(28) Thibon, A.; England, J.; Martinho, M.; Young, V. G.; Frisch, J. R.; Guillot, R.; Girerd, J. J.; Münck, E.; Que, L.; Banse, F. *Angew. Chem. Int. Ed.* **2008,** *47*, 7064-7067.

(29) Sanders-Loehr, J.; Wheeler, W. D.; Shiemke, A. K.; Averill, B. A.; Loehr, T. M. *J. Am. Chem. Soc.* **1989,** *111*, 8084-8093.

(30) (a) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004,** *126*, 6252-6254. (b) Rohde, J.-U.; Betley, T. A.; Jackson, T. A.; Saouma, C. T.; Peters, J. C.; Que, L. *Inorg. Chem.* **2007,** *46*, 5720-5726.

(31) Vogel, C.; Heinemann, F. W.; Sutter, J.; Anthon, C.; Meyer, K. *Angew. Chem., Int. Ed.* **2008,** *47*, 2681-2684.

(32) Jüstel, T.; Müller, M.; Weyhermüller, T.; Kressl, C.; Bill, E.; Hildebrandt, P.; Lengen, M.; Grodzicki, M.; Trautwein, A. X.; Nuber, B.; Wieghardt, K. *Chem.—Eur. J.* **1999,** *5*, 793-810.

(33) Buchler, J. W.; Dreher, C.; Lay, K. L.; Lee, Y. J.; Scheidt, W. R. *Inorg. Chem.* **1983,** *22*, 888-891.

(34) Weckhuysen, B. M.; Wachs, I. E. *J. Chem. Soc., Faraday Trans.* **1996,** *92*, 1969-1973.

(35) Holland, P. L. *Dalton Trans.* **2010,** *39*, 5415-5425.

(36) Brown, E. C.; Bar-Nahum, I.; York, J. T.; Aboelella, N. W.; Tolman, W. B. *Inorg. Chem.* **2007,** *46*, 486-496.

(37) Kincaid, J. R.; Zheng, Y.; Al-Mustafa, J.; Czarnecki, K. *J. Biol. Chem.* **1996,** *271*, 28805-28811.

(38) Green, M. T.; Dawson, J. H.; Gray, H. B. *Science* **2004,** *304*, 1653-1656.

(39) Sitter, A. J.; Reczek, C. M.; Terner, J. *J. Biol. Chem.* **1985,** *260*, 7515-22.

(40) Stone, K. L.; Behan, R. K.; Green, M. T. *Proc. Natl. Acad. Sci. USA* **2005,** *102*, 16563-16565.

(41) Egawa, T.; Miki, H.; Ogura, T.; Makino, R.; Ishimura, Y.; Kitagawa, T. *FEBS Lett.* **1992,** *305*, 206-208.

(42) Stone, K. L.; Behan, R. K.; Green, M. T. *Proc. Natl. Acad. Sci. USA* **2006,** *103*, 12307-12310.

(43) Proshlyakov, D. A.; Henshaw, T. F.; Monterosso, G. R.; Ryle, M. J.; Hausinger, R. P. *J. Am. Chem. Soc.* **2004,** *126*, 1022-1023.

(44) Riggs-Gelasco, P. J.; Price, J. C.; Guyer, R. B.; Brehm, J. H.; Barr, E. W.; Bollinger, J. M.; Krebs, C. *J. Am. Chem. Soc.* **2004,** *126*, 8108-8109.

(45) Yosca, T. H.; Behan, R. K.; Krest, C. M.; Onderko, E. L.; Langston, M. C.; Green, M. T. *J. Am. Chem. Soc.* **2014,** *136*, 9124-9131.

(46) Banerjee, R.; Proshlyakov, Y.; Lipscomb, J. D.; Proshlyakov, D. A. *Nature* **2015,** *518*, 431-434.

(47) Shu, L.; Nesheim, J. C.; Kauffmann, K.; Münck, E.; Lipscomb, J. D.; Que, L. *Science* **1997,** *275*, 515-518.

(48) Magnus, K. A.; Hazes, B.; Ton-That, H.; Bonaventura, C.; Bonaventura, J.; Hol, W. G. J. *Proteins: Struct., Funct., Bioinf.* **1994,** *19*, 302-309.

(49) Loehr, J. S.; Freedman, T. B.; Loehr, T. M. *Biochem. Biophys. Res. Commun.* **1974,** *56*, 510-515.

(50) (a) Huber, K. P.; Herzberg, G., *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules*. Springer US: Boston, MA, 1979. (b) Jules, J. L.; Lombardi, J. R. *J. Phys. Chem. A* **2003,** *107*, 1268-1273. (c) Baudhuin, M. A. A Study of Gas Phase Heterobimetallic and Organometallic Complexes by Anion Photoelectron Spectroscopy. Ph.D. Dissertation, University of Minnesota, Twin Cities, 2016.