

Supporting Information

Preference Behavior on Donating Atoms of an Ambidentate Ligand 2-Methylisothiazol-3(2*H*)-one in its Metal Complexes

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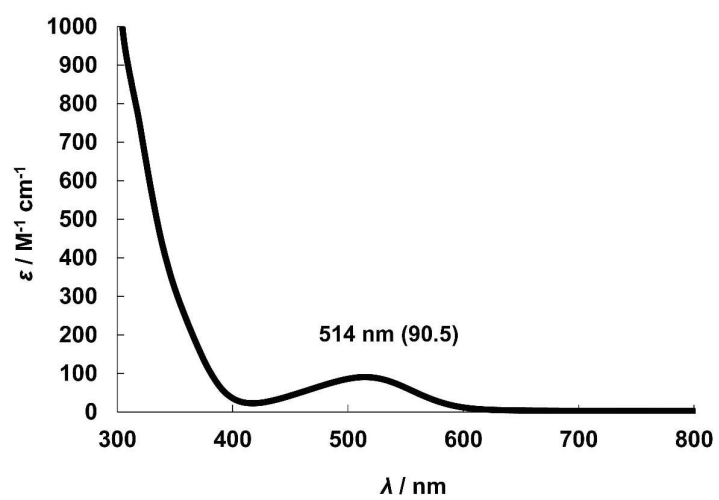


Figure S1. UV-vis absorption spectrum of **1** in aqueous solution.

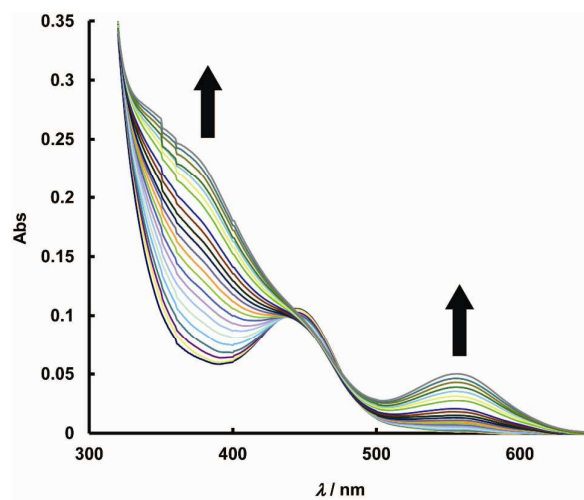


Figure S2. UV-vis spectral changes of **2** by air oxidation. The spectra were recorded for 154200 s. PC was used as a solvent. Two arrows indicate increasing of absorption bands.

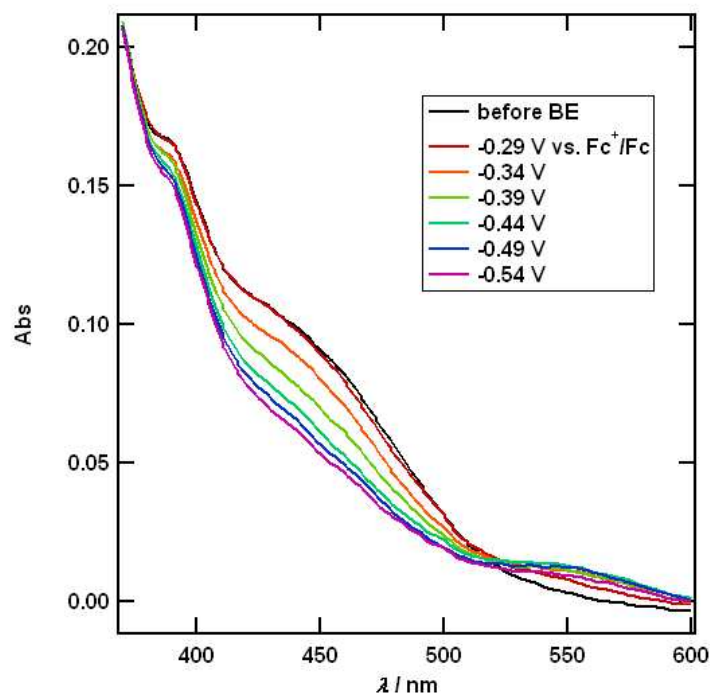


Figure S3. UV-vis absorption spectral changes of **3** by electrochemical reduction in PC containing 0.1 M Bu₄NClO₄.

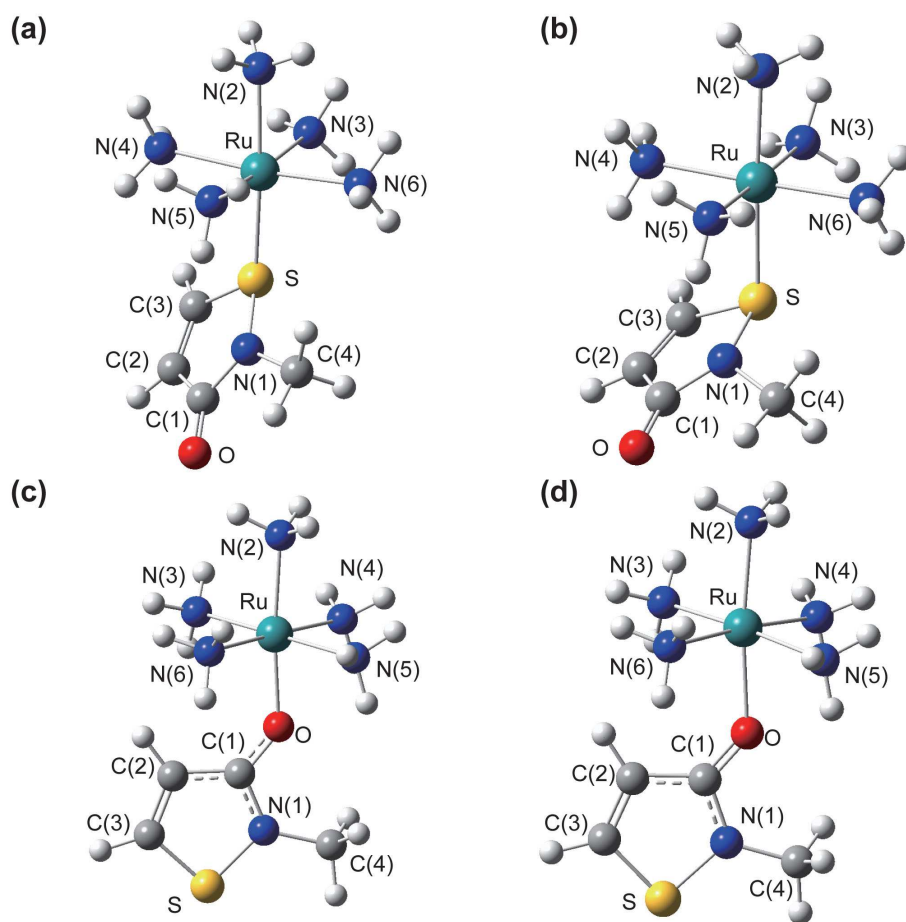


Figure S4. Optimized geometries in the gas phase for (a) $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{MIO-S})]^{3+}$, (b) $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{MIO-S})]^{2+}$, (c) $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{MIO-O})]^{3+}$, and (d) $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{MIO-O})]^{2+}$ at the B3LYP level.

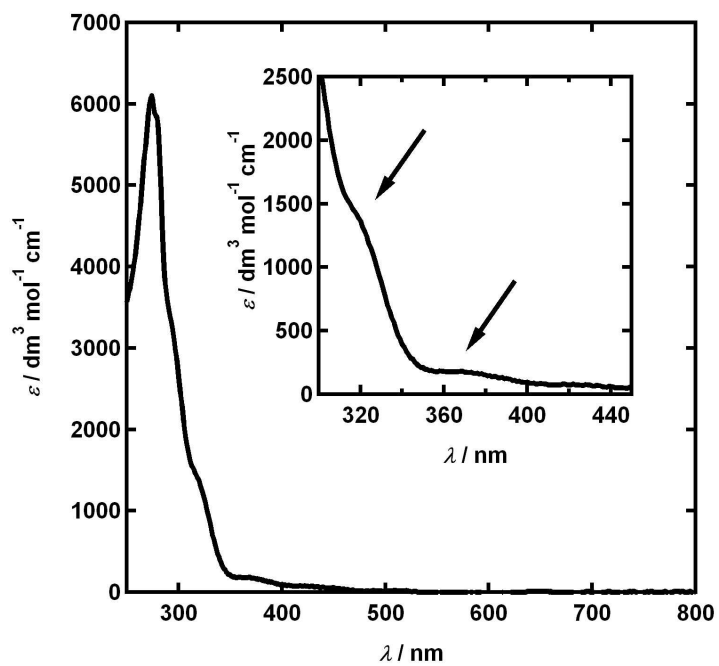


Figure S5. UV-vis absorption spectrum of **4** in CH₃CN. Inset: magnification of the spectrum between 310 nm and 450 nm. Two arrows indicate absorption bands at 317 nm and 365 nm, respectively.

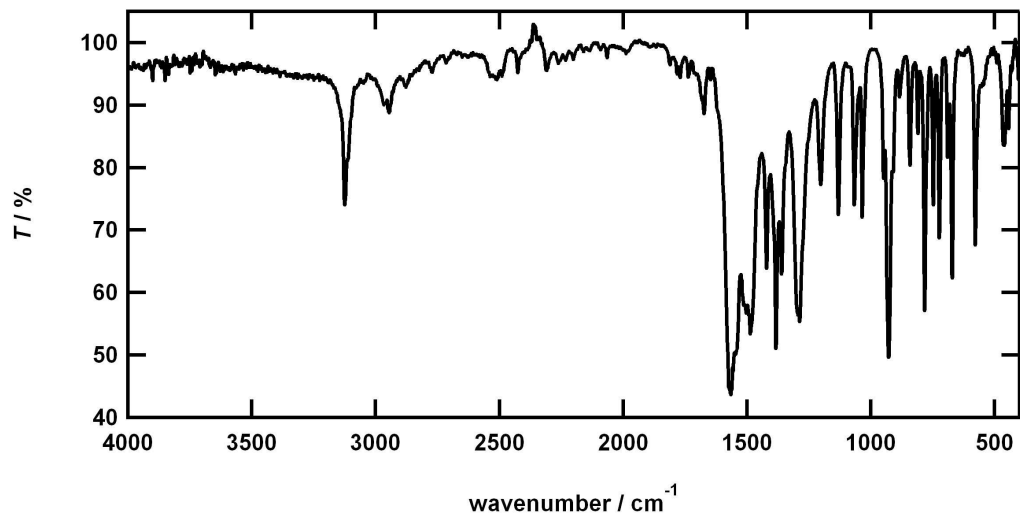


Figure S6. Infrared spectrum of **5** in KBr.

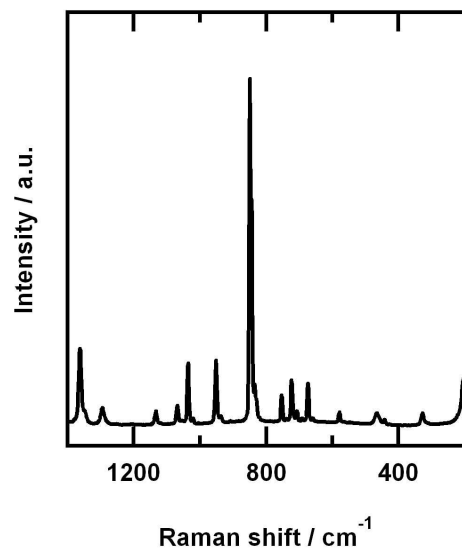


Figure S7. Raman spectrum of **5**.

Table S1. Selected bond lengths (Å) and angles (deg) for the optimized geometries, $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{MIO-O})]^{3+}$ (**Ru^{III}-O**), $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{MIO-O})]^{2+}$ (**Ru^{II}-O**), $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{MIO-S})]^{3+}$ (**Ru^{III}-S**), and $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{MIO-S})]^{2+}$ (**Ru^{II}-S**).

	Ru^{III}-O	Ru^{II}-O	Ru^{III}-S	Ru^{II}-S
Ru-O	2.035	2.175	-	-
Ru-S	-	-	2.319	2.355
Ru-N(2)	2.172	2.175	2.192	2.223
Ru-N(3)	2.179	2.193	2.201	2.208
Ru-N(4)	2.173	2.175	2.194	2.188
Ru-N(5)	2.173	2.175	2.190	2.180
Ru-N(6)	2.179	2.193	2.197	2.202
C(1)-O	1.305	1.270	1.190	1.199
C(1)-C(2)	1.423	1.439	1.479	1.482
C(2)-C(3)	1.371	1.361	1.337	1.333
C(3)-S	1.696	1.706	1.773	1.780
S-N(1)	1.693	1.706	1.668	1.739
N(1)-C(1)	1.360	1.367	1.467	1.434
N(1)-C(4)	1.479	1.467	1.480	1.477
Ru-O-C(1)	138.4	136.4		
Ru-S-N(1)	-	-	125.0	111.3
Ru-S-C(3)	-	-	123.7	112.1
C(3)-S-N(1)	91.6	90.7	93.4	90.7

Table S2. Cartesian coordinates of atoms for the optimized geometry of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{MIO-O})]^{2+}$.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C	1.66747	-0.00341	-0.00503	H	-0.75097	1.933661	-1.59514
C	1.970138	-1.41003	-0.00192	H	-1.90203	1.242248	2.468318
H	1.213515	-2.18108	-0.00246	H	-2.30473	2.318176	1.333288
C	3.308677	-1.65833	0.00243	H	-0.7394	1.942849	1.576028
H	3.811114	-2.61679	0.005314	N	-3.69545	-0.36658	0.007381
Ru	-1.54964	-0.01141	0.000298	N	-1.26675	-1.49754	1.58843
H	-4.16831	0.033654	0.816771	N	-1.27428	-1.50947	-1.57812
H	-4.17437	0.035919	-0.79731	N	-1.68411	1.526808	-1.53187
H	-3.96353	-1.35017	0.006981	N	-1.67461	1.539414	1.520454
H	-0.33583	-1.41994	1.996087	N	2.826358	0.721254	-0.00955
H	-1.90978	-1.39932	2.373509	O	0.542008	0.585635	-0.00422
H	-1.35483	-2.47426	1.31011	S	4.242489	-0.23045	0.001244
H	-1.35606	-2.48432	-1.2915	C	2.892968	2.186544	0.003383
H	-0.34712	-1.4315	-1.99419	H	2.302429	2.588663	-0.81922
H	-1.92419	-1.42012	-2.3586	H	2.521774	2.57521	0.952362
H	-1.91402	1.220692	-2.4763	H	3.927353	2.499899	-0.12468
H	-2.31656	2.304712	-1.34896				

Table S3. Cartesian coordinates of atoms for the optimized geometry of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{MIO}-\text{O})]^{3+}$.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C	-1.63968	-0.05173	-0.00632	H	0.813039	2.030074	1.567167
C	-1.97855	-1.43387	-0.00234	H	1.977138	1.217999	-2.45117
H	-1.26455	-2.24471	-0.00424	H	2.389779	2.273496	-1.2985
C	-3.3361	-1.62793	0.002059	H	0.822239	1.992968	-1.61934
H	-3.88056	-2.56518	0.004612	N	3.633307	-0.38505	0.012909
Ru	1.492767	-0.01506	0.000305	N	1.246947	-1.53268	-1.5441
H	4.121313	0.027935	-0.78443	N	1.23365	-1.51106	1.563467
H	4.107527	0.009522	0.827743	N	1.711657	1.551688	1.490377
H	3.903554	-1.37002	0.004361	N	1.724992	1.528612	-1.51168
H	0.338389	-1.45388	-2.00435	N	-2.75318	0.729785	-0.0069
H	1.926509	-1.47083	-2.30465	O	-0.46929	0.525086	-0.01069
H	1.304242	-2.50405	-1.23614	S	-4.19145	-0.16358	0.000773
H	1.304638	-2.48629	1.270865	C	-2.78509	2.208411	0.003948
H	0.31701	-1.43396	2.00768	H	-2.38903	2.581417	0.947941
H	1.9001	-1.43208	2.333931	H	-2.21194	2.592305	-0.83825
H	1.935591	1.253366	2.440914	H	-3.81691	2.539663	-0.09864
H	2.392579	2.283131	1.281603				

Table S4. Cartesian coordinates of atoms for the optimized geometry of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{MIO-S})]^{2+}$.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H	1.2039	-2.60825	-1.13228	H	-0.46878	0.73327	2.648168
H	3.459867	-2.45215	0.219455	H	-3.18187	0.836353	1.85384
C	1.661576	-1.72287	-0.70956	H	-3.91323	0.694465	0.425101
C	2.800951	-1.62783	-0.02452	H	-3.63353	-0.61936	1.320617
S	0.886547	-0.14533	-0.98997	N	-0.30683	1.121531	1.719606
C	3.177869	-0.23881	0.330263	N	-3.2077	0.255799	1.016226
O	4.188878	0.14391	0.848891	N	-2.17412	-1.11496	-1.56124
N	2.12626	0.652046	-0.06724	Ru	-1.20948	0.014753	0.072008
H	1.659823	2.713613	-0.28322	H	-2.50616	1.946629	-1.44877
C	2.497288	2.032097	-0.44074	H	-1.4005	2.717667	-0.56322
H	3.315595	2.3279	0.214057	H	-0.95678	1.935885	-1.90446
H	2.832446	2.09437	-1.4781	H	-1.35249	-2.64283	0.861356
H	-1.9533	-0.7575	-2.49011	H	0.073211	-2.04709	1.337563
H	-1.92261	-2.1019	-1.6038	H	-1.26431	-1.75308	2.20314
H	-3.19265	-1.11204	-1.51528	N	-1.55813	1.855977	-1.08452
H	0.708027	1.118318	1.593043	N	-0.91381	-1.80721	1.24709
H	-0.57133	2.102795	1.800778				

Table S5. Cartesian coordinates of atoms for the optimized geometry of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{MIO-S})]^{3+}$.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H	1.353951	-2.74351	-0.63483	H	-0.94068	0.633871	2.706516
H	3.854029	-2.36084	0.167118	H	-3.43745	0.373583	1.699933
C	1.843262	-1.81141	-0.38322	H	-3.82658	1.008347	0.273112
C	3.103549	-1.59337	0.005424	H	-3.91709	-0.5916	0.493749
S	0.960291	-0.28837	-0.59476	N	-0.68431	1.107804	1.838573
C	3.436844	-0.16444	0.19305	N	-3.33072	0.220741	0.695288
O	4.468493	0.345532	0.496208	N	-2.00499	-1.04976	-1.74538
N	2.238781	0.641563	-0.06439	Ru	-1.25308	0.013364	0.028669
H	1.498966	2.633077	0.044692	H	-2.39805	2.004291	-1.51645
C	2.374962	2.094025	-0.31499	H	-1.34235	2.743973	-0.54668
H	3.24841	2.42472	0.247005	H	-0.83147	1.985012	-1.87736
H	2.54261	2.291971	-1.37552	H	-1.32418	-2.70333	0.640343
H	-1.4664	-0.87451	-2.5953	H	-0.38016	-1.99119	1.740655
H	-2.03711	-2.0676	-1.67059	H	-1.98594	-1.90782	1.871799
H	-2.96019	-0.7888	-1.997	N	-1.476	1.890834	-1.09133
H	0.31933	1.267579	1.930456	N	-1.22771	-1.84827	1.189812
H	-1.1038	2.03524	1.923797				