Supplementary Material

Contents

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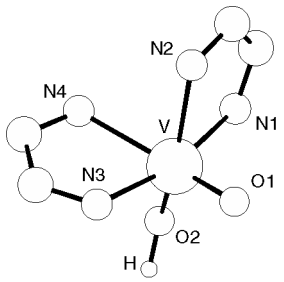
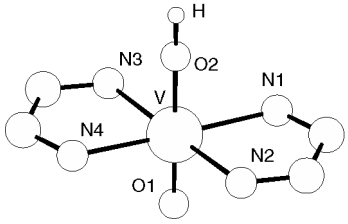
Table S1. Selected bond distances (Å) and bond angles (deg) calculated for the *cis*- and *trans*- isomers of the model complexes $[V^{IV}OX(L)_2]^{n+}$, X = OH^-, **2m**, SO_4^{2-}, **3m** and Cl^-, **4m**.[a]

	2m-cis	**2m-trans**	**3m-cis**	**3m-trans**	**4m-cis**	**4m-trans**
V–O1	1.691	1.632	1.605	1.624	1.592	1.606
V–X[b]	1.798	1.824	1.898	1.951	2.322	2.460
V–N1	2.123	2.159	2.109	2.151	2.117	2.116
V–N2	2.217	2.159	2.162	2.134	2.147	2.116
V–N3	2.094	2.159	1.977	2.138	2.108	2.116
V–N4	2.263	2.159	2.248	2.138	2.316	2.116
O1–V–X	109.8	180.0	107.5	164.3	105.2	180.0
O1–V–N3	90.5	90.9	93.7	93.6	92.8	95.8
X–V–N3	97.2	89.1	96.4	78.3	92.6	84.2
O1–V–N1	102.1	90.9	101.7	92.7	102.1	95.8
X–V–N1	84.6	89.1	86.6	78.1	87.3	84.2
N3–V–N1	165.8	104.6	157.5	111.1	164.5	102.7
O1–V–N2	90.3	90.9	89.1	95.8	92.0	95.8
X–V–N2	153.1	89.1	155.9	94.2	156.3	84.2
N3–V–N2	100.3	178.1	91.5	168.2	100.2	168.5
N1–V–N2	73.5	75.4	72.7	75.6	75.1	76.0
O1–V–N4	160.0	90.9	163.5	95.0	62.3	95.8
X–V–N4	85.5	89.1	86.8	95.9	83.4	84.2
N3–V–N4	74.4	75.4	74.3	75.6	72.2	76.0
N1–V–N4	91.8	178.1	87.1	169.5	92.4	168.5
N2–V–N4	79.8	104.6	80.2	96.4	81.8	102.7
X–H	0.974	0.968				
X-S			1.656	1.790		
V–X–H	134.9	180.0				
V-X-S			140.8	131.6		

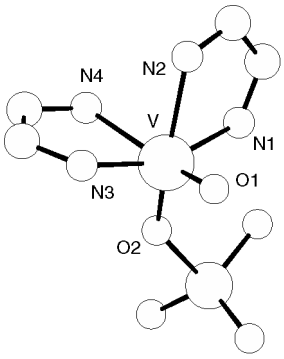
[a] Numbering scheme as in Figure S1. [b] X=O2 for **2m**, **3m** and Cl for **4m**.



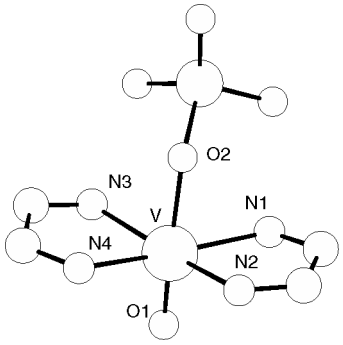
2m-cis



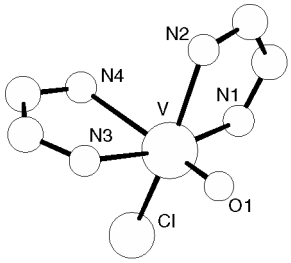
2m-trans



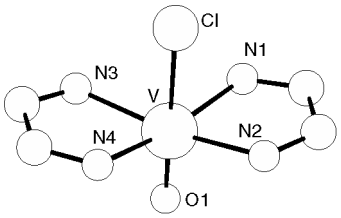
3m-cis



3m-trans



4m-cis



4m-trans

Figure S1. Optimized geometries of for the *cis*- and *trans*- isomers of the model complexes $[V^{IV}O(OH)(L)_2]^+$, **2m**, $[V^{IV}O(SO_4)(L)_2]$, **3m**, and $[V^{IV}OCl(L)_2]^+$, **4m,** (hydrogens not shown).

Figure S2

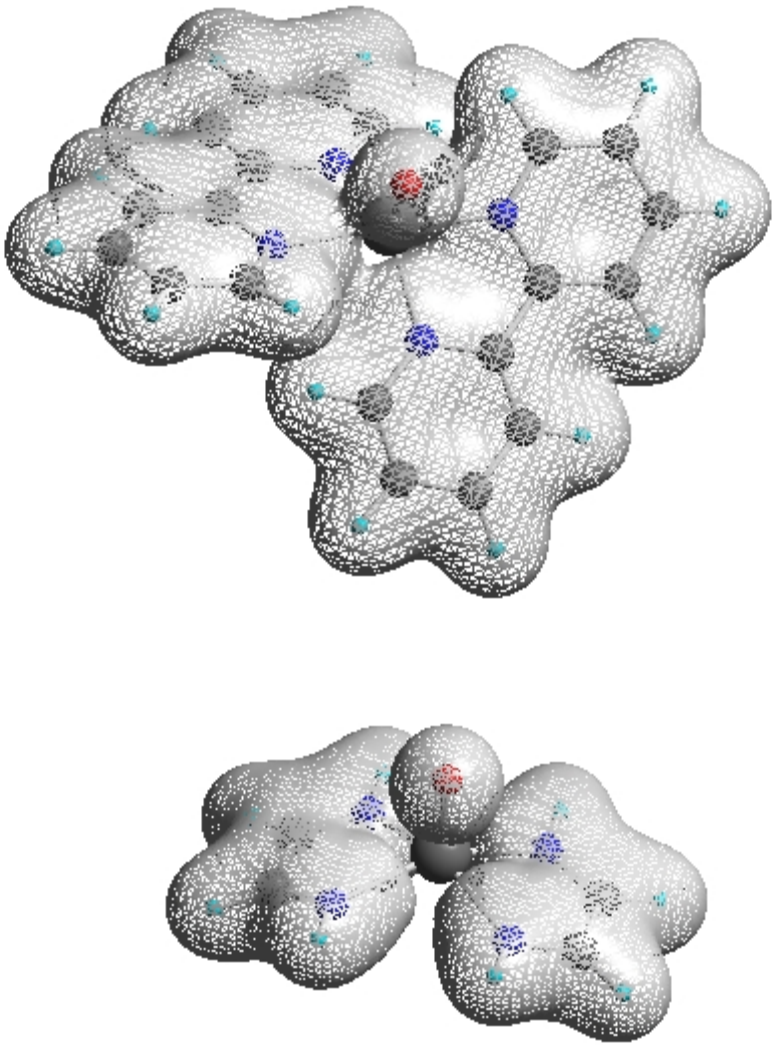


Figure S2. Total charge density map for the optimized trigonal bipyramidal structure of $[V^{IV}O(bipy)_2]^{2+}$, **1** (isocharge 0.005 au).