

Supporting Information

Spectroscopic and DFT Study on the Complexation of Np(V) with Amidoxime-Derived Ligands in Aqueous Solutions: Speciation and Structural Optimization[†]

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Table S1. Bond lengths and WBIs in Np(V)-BzAO complexes with different coordination modes.

Bond parameters	Bonds	Np(V)-BzAO complexes			
		NpL _a	NpL _b	NpL _c	NpL _d
Bond length (Å)	M-N	2.453	2.442	2.565	2.443
	M-O	2.368	2.367		
WBIs	M-N	0.370	0.383	0.325	0.379
	M-O	0.507	0.523		
ΔG (kcal·mol ⁻¹)		-16.2	101.5	117.5	132.3

Table S2. Bond lengths and WBIs in Np(V)-Py-2-AO complexes with different coordination modes.

Bond parameters	Bonds	Np(V)- Py-2-AO complexes			
		NpL _a	NpL _b	NpL _c	NpL _d
Bond length (Å)	M-N _{Pyridine}			2.699	2.747
	M-N _{Oxime}	2.660	2.725	2.569	2.548
WBIs	M-N _{Pyridine}			0.267	0.258
	M-N _{Oxime}	0.310	0.297	0.340	0.354
ΔG (kcal·mol ⁻¹)		237.3	261.4	-43.7	234.5

Table S3. Bond lengths and WBIs in Np(V)-Py-3-AO complexes with different coordination modes.

Bond parameters	Bonds	Np(V)-Py-3-AO complexes			
		NpL _a	NpL _b	NpL _c	NpL _d
Bond length (Å)	M-N	2.467	3.161	2.542	2.652
	M-O	2.367	2.294		
WBIs	M-N	0.386	0.032	0.369	0.321
	M-O	0.490	0.586		
ΔG (kcal·mol ⁻¹)		-36.7	126.5	104.1	156.1

The coordinates of optimized structures of complexes by DFT method

Table S4 NpL_{BzAOa}

O	-2.49474900	7.97039700	-0.19045400
Np	-3.70038600	5.67273200	0.03513400
O	-3.96710400	6.00003600	1.79507700
O	-1.14167200	5.06381700	0.24077400
O	-3.38848400	5.53051100	-1.74057800
O	-6.23081000	6.30145000	-0.05971500
H	-1.40033500	4.27601300	0.75864400
H	-1.11019900	4.72344700	-0.67125300
H	-6.32667500	6.38250200	0.90524600
H	-6.72162600	5.49191000	-0.29017100
H	-1.84281400	8.09538100	0.51833200
H	-1.99220400	7.93230300	-1.02040900
C	-9.55776300	2.40087500	-0.05138700
C	-8.83835800	1.46603700	-0.79915900
C	-7.44574100	1.42350000	-0.72571200
C	-6.74918800	2.32148000	0.09918100
C	-7.48280600	3.24387500	0.86874000
C	-8.87446800	3.28821900	0.78537100
C	-5.27473800	2.30130000	0.15886700
N	-4.63914100	3.42190000	0.30213800
O	-3.27588200	3.36358400	0.35056100
N	-4.59904600	1.10428100	-0.03224000
H	-10.64218800	2.43114600	-0.11069900
H	-6.88522200	0.71344900	-1.32619700
H	-6.94760700	3.88683800	1.56166400
H	-9.42918200	3.99907300	1.39266800
H	-4.99251300	0.30536800	0.45096500
H	-3.60533600	1.23310900	0.13836400
H	-9.36286200	0.77156500	-1.45014900

Table S5 NpL_{BzAOB}

C	-9.26878600	2.72935800	0.24174600
C	-8.72547300	1.88321300	-0.72835900
C	-7.36571100	1.57155800	-0.71364500
C	-6.52525300	2.10615500	0.27625800
C	-7.08507000	2.93457400	1.26864900
C	-8.44445900	3.25146800	1.24231900
C	-5.07973100	1.80966700	0.28275200
N	-4.25789800	2.74574500	0.64016000
O	-2.93010000	2.44351900	0.66225800
N	-4.62832500	0.58021800	-0.17459600
H	-10.32830400	2.96904300	0.22653700

H	-6.93909200	0.93323400	-1.48146700
H	-6.45322600	3.27530900	2.08536400
H	-8.86497200	3.88434000	2.01949700
H	-5.16383000	-0.22003100	0.14102300
H	-3.62967100	0.48899400	-0.00799600
H	-9.36216800	1.47009200	-1.50623300
O	-2.56071400	7.27431300	1.44409000
Np	-2.96568400	4.78736500	0.99491700
O	-3.21937100	4.64537600	2.79812800
O	-0.56130800	3.79554200	1.01579800
O	-2.77482900	5.11507700	-0.77912800
O	-5.41947700	5.74929300	0.62770300
O	-4.50854200	7.12600400	3.24785500
H	-0.94901200	2.91173200	1.17265100
H	-0.34625700	3.79179200	0.06741900
H	-4.12480200	6.23867500	3.43692600
H	-5.21683200	6.91927500	2.61308400
H	-3.23097300	7.48324400	2.15654700
H	-2.66536500	7.92292300	0.73250300
H	-5.96977900	4.94283100	0.67933300
H	-5.32868400	5.92430300	-0.32549400

Table S6 NpL_{BzAOc}

C	-9.29048200	2.68337400	0.09278900
C	-8.54635200	2.40966500	-1.05688900
C	-7.19030700	2.09304600	-0.95751200
C	-6.57225800	2.05085700	0.30105700
C	-7.32416300	2.32100700	1.45934000
C	-8.67944900	2.63729900	1.35041300
C	-5.12794900	1.73135000	0.41834600
N	-4.43639300	2.45664000	1.26758700
O	-3.03686500	2.05510400	1.25349500
N	-4.60631500	0.75626400	-0.34012500
H	-10.34607100	2.92438300	0.01143700
H	-6.60885200	1.90765500	-1.85619900
H	-6.85133800	2.24212800	2.43407600
H	-9.26277400	2.82614100	2.24679500
H	-5.20709300	0.11196800	-0.83225700
H	-3.62072600	0.54380100	-0.25781900
H	-9.01877200	2.44741200	-2.03368900
O	-1.66351700	6.83183200	0.69359700
Np	-3.28580100	4.74910300	1.30840700
O	-2.90715800	4.46547000	3.03979300

O	-0.79795400	4.25108700	0.87305300
O	-3.66485500	5.07865100	-0.41792600
O	-5.92914900	5.29920900	1.26458500
O	-4.09367500	7.05433200	2.28525100
H	-0.32184300	3.89599500	1.64146600
H	-0.41828200	5.13463200	0.70992900
H	-3.99412900	6.96876300	3.24925600
H	-5.05402900	7.00117800	2.11749200
H	-1.88612900	7.61767400	1.22159800
H	-2.01490000	7.01170300	-0.19645100
H	-6.55272700	4.59477300	1.52140500
H	-5.97182200	5.33374600	0.29212000
H	-2.84127100	1.91536100	2.19987900

Table S7 NpL_{BzAOd}

C	-9.26879000	2.72929000	0.24201200
C	-8.72556600	1.88321800	-0.72820700
C	-7.36579000	1.57161400	-0.71368000
C	-6.52523000	2.10619000	0.27614800
C	-7.08495400	2.93454100	1.26865000
C	-8.44435800	3.25138400	1.24250600
C	-5.07970100	1.80972900	0.28248800
N	-4.25785800	2.74579400	0.63990600
O	-2.93005700	2.44357700	0.66195100
N	-4.62831300	0.58031200	-0.17496800
H	-10.32832000	2.96893000	0.22695200
H	-6.93924400	0.93334200	-1.48158600
H	-6.45301800	3.27525900	2.08530100
H	-8.86479700	3.88419800	2.01977100
H	-5.16378000	-0.21996300	0.14065000
H	-3.62964500	0.48909200	-0.00844700
H	-9.36234300	1.47011200	-1.50602100
O	-2.56077800	7.27425800	1.44434100
Np	-2.96564700	4.78738800	0.99485900
O	-3.21963900	4.64527300	2.79802100
O	-0.56130000	3.79550600	1.01592400
O	-2.77445700	5.11520900	-0.77912700
O	-5.41942600	5.74928500	0.62755500
O	-4.50872900	7.12586100	3.24795200
H	-0.94906100	2.91168900	1.17259700
H	-0.34618000	3.79190800	0.06756000
H	-4.12502700	6.23849100	3.43691500
H	-5.21699900	6.91923700	2.61312500

H	-3.23109700	7.48313600	2.15675900
H	-2.66532000	7.92296000	0.73282400
H	-5.96968800	4.94279700	0.67920900
H	-5.32879000	5.92438100	-0.32563800

Table S8 NpL_{Py-2-AOa}

O	0.63547500	4.42895200	-2.12838300
Np	-1.23131100	2.89524000	-1.24502000
O	-0.25311800	2.59835700	0.25148500
O	0.59541800	1.52258500	-2.50086400
O	-2.19447100	3.13714500	-2.73124400
O	-3.31357400	2.59313800	0.13778300
O	-1.76705500	5.25386400	-0.43568800
H	0.66764600	0.72466800	-1.93315000
H	0.33670100	1.20462500	-3.38148600
H	-1.34539000	5.56926900	0.38020400
H	-2.69585500	5.53566400	-0.40124500
H	1.45258000	3.93439800	-2.30944200
H	0.44945400	4.95626000	-2.92236900
H	-3.10298400	2.33993300	1.05142700
H	-3.74484100	1.78828500	-0.28431900
C	-6.13674900	-0.24179300	-2.69006500
C	-5.40641800	-1.35805300	-3.08853700
C	-4.12345100	-1.54564400	-2.57138200
C	-3.61722600	-0.60620000	-1.66838300
N	-4.32309900	0.47359000	-1.28291900
C	-5.54977800	0.64800000	-1.78877700
C	-2.25104400	-0.78291800	-1.09098100
N	-1.51392300	0.27324700	-0.89460100
O	-0.23120800	-0.10710700	-0.37433400
N	-1.81780500	-2.04795000	-0.86601800
H	-7.13663800	-0.05537200	-3.06698400
H	-6.08139700	1.53447700	-1.45373300
H	-2.49869400	-2.78062600	-0.72559200
H	-0.93249600	-2.14496800	-0.38373700
H	-5.82014000	-2.06997300	-3.79608400
H	-3.51624600	-2.38868500	-2.88344600
H	-0.01156400	0.67499300	0.18698400

Table S9 NpL_{Py-2-AOb}

O	0.90048700	4.50033100	-1.92664700
Np	-1.12254000	2.93883500	-1.41038000

O	-0.56543900	2.89103200	0.30732000
O	0.91962800	1.86448700	-2.03621000
O	-1.73887000	3.04128000	-3.10010100
O	-3.36407500	2.73385100	-0.01552300
O	-2.18511000	5.23821700	-0.64434200
H	0.45706800	0.59308700	-1.30663800
H	0.90240500	1.61211100	-2.97340100
H	-1.61001700	5.41624100	0.11922200
H	-2.96187900	4.77874800	-0.26938000
H	1.31880900	3.59332900	-1.99632200
H	0.81828700	4.81068000	-2.84299200
H	-2.82054700	2.45915900	0.74470400
H	-3.72327100	1.88719900	-0.41736100
C	-6.27189300	-0.21342300	-2.48124500
C	-5.61196900	-1.37825500	-2.87097000
C	-4.28713700	-1.56580400	-2.48760900
C	-3.64844300	-0.57986700	-1.71866600
N	-4.29458800	0.53766300	-1.33544200
C	-5.56571700	0.71334600	-1.71789000
C	-2.22943400	-0.77457700	-1.32757400
N	-1.41025500	0.23215300	-1.27743800
O	-0.12570000	-0.18383100	-0.94833400
N	-1.79659400	-2.07936300	-1.17690200
H	-7.30323300	-0.02296100	-2.75910600
H	-6.03460400	1.63724100	-1.38751100
H	-2.42903600	-2.70562900	-0.69566200
H	-0.83617900	-2.12348900	-0.85270000
H	-6.11698000	-2.12673200	-3.47494000
H	-3.73067500	-2.44285500	-2.79756400

Table S10 NpL_{Py-2-AOc}

C	-5.64557000	0.11836700	-3.02828700
C	-5.33409300	-1.21525400	-2.78090000
C	-4.19059500	-1.51312700	-2.03686000
C	-3.40676600	-0.46080700	-1.56541000
N	-3.69571000	0.83542200	-1.81742200
C	-4.79149600	1.10782600	-2.53569100
C	-2.19059700	-0.68374600	-0.73617600
N	-1.32684800	0.28974200	-0.76904200
O	-0.24474900	0.10002000	0.15389800
N	-2.04284400	-1.81920300	-0.02798700
H	-6.52506400	0.39647000	-3.59900800
H	-4.99146300	2.15937400	-2.71501100

H	-2.83906000	-2.40110200	0.18513900
H	-1.23062800	-1.88860500	0.57249600
H	-5.96172400	-2.01387800	-3.16379000
H	-3.90177900	-2.54318000	-1.85551900
O	-0.57890900	5.01032700	-1.48401100
Np	-1.71556600	2.70859900	-1.47033400
O	-1.66724700	2.84359400	0.32680300
O	0.78943600	2.10231600	-1.51800700
O	-1.69229100	2.66551400	-3.25979200
O	-3.80085400	4.22097800	-1.49807800
H	0.85190300	1.30728700	-0.94445600
H	1.05582900	1.80893400	-2.40559000
H	-4.05702600	4.62338000	-0.65156600
H	-3.88202000	4.91586800	-2.17204900
H	-0.12460900	5.23358200	-0.65447900
H	0.02961200	5.24574700	-2.20360000
H	-0.42177300	0.80345500	0.81592900

Table S11 NpL_{Py-2-AOd}

C	-5.80267900	-0.15389700	-2.88902300
C	-5.43338000	-1.43500100	-2.48580000
C	-4.22229000	-1.61281200	-1.81965200
C	-3.41548000	-0.49824500	-1.56396200
N	-3.77372600	0.74563900	-1.96030200
C	-4.93169100	0.89999000	-2.61005600
C	-2.12512400	-0.62123400	-0.85406500
N	-1.32927200	0.39301000	-0.94237500
O	-0.15675400	0.26829400	-0.24148000
N	-1.79646000	-1.79563600	-0.20078800
H	-6.73381300	0.03232800	-3.41338300
H	-5.17388500	1.91359300	-2.92223400
H	-2.54812600	-2.22038900	0.32960600
H	-0.94679800	-1.68866300	0.34530200
H	-6.07200100	-2.28826000	-2.69535300
H	-3.88617800	-2.60187100	-1.52868300
O	-0.39985800	5.13793800	-1.53550100
Np	-2.03439000	2.77707600	-1.59196500
O	-2.53182900	2.94284900	0.13559800
O	0.28816900	2.67190400	-1.01188200
O	-1.61713300	2.69474400	-3.34608900
O	-3.14802200	5.17232700	-1.62466300
H	0.22448500	1.21015200	-0.38020500
H	0.78681900	2.47265900	-1.82143600

H	-3.45927600	5.16088300	-0.70322300
H	-2.23260200	5.53208800	-1.55990800
H	0.08556600	4.33310500	-1.16059800
H	-0.09337300	5.18672800	-2.45598100

Table S12 NpL_{Py-3-AOa}

O	-2.46888000	7.97515000	-0.13367900
Np	-3.67312700	5.67810400	0.02803900
O	-3.93701600	5.98599500	1.79109500
O	-1.12735600	5.02881300	0.21714500
O	-3.37075200	5.55069100	-1.74917800
O	-6.17320900	6.39833500	-0.10159200
H	-1.38430600	4.23020600	0.71851800
H	-1.09130000	4.70907000	-0.70207700
H	-6.33041200	6.42369900	0.85790100
H	-6.70379800	5.65188800	-0.42933800
H	-1.86416300	8.12011900	0.61202000
H	-1.92422400	7.99067200	-0.93704600
C	-9.50668900	2.31352500	-0.02588600
N	-8.83077700	1.40425000	-0.73845400
C	-7.49626500	1.42265400	-0.65990800
C	-6.76562800	2.33256400	0.12418800
C	-7.49856300	3.26140500	0.88104800
C	-8.88788800	3.26058900	0.79534400
C	-5.29321500	2.30788400	0.15302800
N	-4.65248700	3.42824600	0.28208800
O	-3.29086400	3.35927500	0.31264900
N	-4.62712100	1.10771900	-0.04579300
H	-10.59173600	2.27765100	-0.10756500
H	-6.96653300	0.68746900	-1.26212800
H	-6.97022300	3.93906200	1.54578900
H	-9.48636000	3.95934300	1.37316600
H	-5.01401900	0.30856500	0.44201900
H	-3.62932800	1.23159000	0.10235800

Table S13 NpL_{Py-3-AOb}

O	-0.48561500	4.96825100	-1.07865100
Np	-0.46897900	2.43655600	-0.89390200
O	0.15810200	2.56419000	0.79026100
O	1.93910800	2.01399100	-1.64456500
O	-0.99438700	2.44095600	-2.63321300
O	-2.99626000	2.93331800	-0.38647400

O	-2.68039300	4.77086500	-2.53908800
H	2.65898000	2.25240700	-1.03998300
H	2.21461300	2.25976000	-2.54146800
H	-3.16261700	4.28994100	-1.83549900
H	-2.24894800	4.02981200	-3.01422900
H	-0.58451400	5.48734900	-0.26628900
H	-1.30262300	5.12636100	-1.64631300
H	-3.14279300	2.98735600	0.57241300
H	-3.23501200	1.96245900	-0.63225400
C	-7.20661600	-1.53616900	-2.48907400
N	-6.21995400	-2.28004800	-3.00207600
C	-4.97367900	-2.01371100	-2.59737800
C	-4.64142700	-1.01527000	-1.66571800
C	-5.69536900	-0.25300800	-1.14012900
C	-6.99413300	-0.51066400	-1.56354400
C	-3.24069200	-0.79282300	-1.26138300
N	-2.87215100	0.38333000	-0.85114800
O	-1.55936300	0.46816200	-0.44689400
N	-2.33196700	-1.82830800	-1.39229200
H	-8.21310300	-1.77206100	-2.83115500
H	-4.18555000	-2.61188600	-3.05015900
H	-5.48611300	0.51766500	-0.40533400
H	-7.83238300	0.06062700	-1.17544000
H	-2.68056000	-2.74873900	-1.15513000
H	-1.45490500	-1.58616800	-0.93889100

Table S14 NpL_{Py-3-AOc}

O	1.40483400	3.63915000	-1.38459200
Np	-1.00122100	2.78578700	-1.09475100
O	-0.65423400	2.58377700	0.64789400
O	0.41037700	0.72527000	-1.51228000
O	-1.30372000	2.94987600	-2.85838000
O	-3.31655000	3.56648400	-0.13718200
O	-1.10679000	5.36387400	-1.17163300
H	0.98871300	0.41177400	-0.79796600
H	0.88942800	0.58572000	-2.34512100
H	-1.34335900	5.97154600	-0.45246900
H	-1.64825900	5.62269300	-1.93700400
H	1.84955500	3.95190900	-0.57928900
H	1.55821800	4.31722300	-2.06333900
H	-3.16391600	3.97515800	0.73118600
H	-3.68857400	2.68191700	0.08185200
C	-6.12805900	-2.87871300	-1.78028500

N	-4.98250300	-3.09585800	-2.43757400
C	-4.10549200	-2.09355500	-2.49504400
C	-4.31403500	-0.83685500	-1.89906900
C	-5.51515100	-0.63058900	-1.20464800
C	-6.43755400	-1.66994800	-1.15037300
C	-3.26921700	0.20455500	-2.06350300
N	-2.76434700	0.95470000	-1.10732700
O	-3.44409600	0.78869700	0.14693400
N	-2.74636700	0.34683200	-3.30572300
H	-6.83084000	-3.70882400	-1.75823700
H	-3.17494400	-2.30082200	-3.02109000
H	-5.72779300	0.32113000	-0.73299200
H	-7.38339100	-1.54767800	-0.63268200
H	-3.27960100	-0.01952200	-4.08149100
H	-2.17666200	1.17273700	-3.48761700
H	-2.72195400	0.62565500	0.78239300

Table S15 NpL_{Py-3-Aod}

O	0.98902100	4.39178700	-2.03036800
Np	-1.01825100	2.85404700	-1.25288800
O	0.04743900	2.13573000	0.02700300
O	0.56577900	1.04150900	-2.45101400
O	-1.92097500	3.60065400	-2.62787200
O	-2.54082800	3.48733800	0.42817500
O	-1.00755300	5.41701000	-0.32474800
H	1.02423700	1.03233700	-1.58718000
H	1.22556500	1.30228500	-3.11316100
H	-1.68725100	4.88978600	0.21399200
H	-1.56193700	5.86595400	-0.98527600
H	0.77297900	5.00792300	-1.29933300
H	0.61656000	4.82324500	-2.81782700
H	-2.24528000	3.13967600	1.28494400
H	-3.57998900	2.28238100	-0.05986300
C	-6.54490500	-2.56778300	-1.86241600
N	-5.35653000	-3.17214700	-1.74362900
C	-4.27517600	-2.38851700	-1.68669800
C	-4.31281000	-0.98428100	-1.74002400
C	-5.57144800	-0.37353200	-1.85532100
C	-6.70200600	-1.18150800	-1.92148000
C	-3.04222600	-0.21715000	-1.72238100
N	-2.85441900	0.94210500	-1.17307500
O	-3.94999200	1.43774800	-0.46183600
N	-1.95371400	-0.85597700	-2.30638900

H	-7.41231100	-3.22442600	-1.91118900
H	-3.31961900	-2.89612700	-1.57537800
H	-5.64907200	0.70556700	-1.88674200
H	-7.69190000	-0.74524000	-2.01625800
H	-2.16709600	-1.34189600	-3.16954200
H	-1.09769400	-0.31119700	-2.36622500