Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Elucidating cation–cation interactions in neptunyl dications using multireference ab initio theory

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S1 XYZ Coordinates in Angstroms

S1.1 T-shaped $[NpO_2]_2^{2+}$ (quintet state) in aqueous solution

Np	0.0000000	0.0000000	−2.1239825
O	1.7811044	0.0000000	−2.1376484
O	−1.7811044	0.0000000	−2.1376484
Np	0.0000000	0.0000000	2.0860230
O	0.0000000	0.0000000	0.2451645
O	0.0000000	0.0000000	3.8564210

S1.2 T-shaped $[NpO_2]_2^{2+}$ (quintet state) and 3 H_2O in aqueous solution

Np	0.0000000	0.0000000	−2.0162786
O	0.0000000	1.7993662	−1.9936034
O	0.0000000	−1.7993662	−1.9936034
Np	0.0000000	0.0000000	2.2381797
O	0.0000000	0.0000000	0.3847404
O	0.0000000	0.0000000	4.0266122
H	−2.9808418	0.7801522	2.4106679
H	−2.9808418	−0.7801522	2.4106679
O	−2.4442685	0.0000000	2.1759493
H	2.9808418	0.7801522	2.4106679
H	2.9808418	−0.7801522	2.4106679
O	2.4442685	0.0000000	2.1759493
O	0.0000000	0.0000000	−4.4925744
H	0.7813539	0.0000000	−5.0740214
H	−0.7813539	0.0000000	−5.0740214

S1.3 T-shaped $[NpO_2]_2^{2+}$ (quintet state) and 4 H_2O in aqueous solution

Np	0.0000000	0.0000000	−1.7831053
O	−0.0000000	1.8016877	−1.8203463
O	−0.0000000	−1.8016877	−1.8203463
Np	0.0000000	0.0000000	2.4528528
O	0.0000000	0.0000000	0.5839093
O	0.0000000	0.0000000	4.2469094
H	−2.9653457	0.7777507	2.7278525
H	−2.9653457	−0.7777507	2.7278525
O	−2.4617443	0.0000000	2.4215408
H	2.9653457	0.7777507	2.7278525
H	2.9653457	−0.7777507	2.7278525
O	2.4617443	0.0000000	2.4215408
O	2.2177259	0.0000000	−2.7462833
H	2.7238956	0.7827571	−3.0304497
H	2.7238956	−0.7827571	−3.0304497
O	−2.2177259	0.0000000	−2.7462833
H	−2.7238956	0.7827571	−3.0304497
H	−2.7238956	−0.7827571	−3.0304497

S1.4 T-shaped $[NpO_2]_2^{2+}$ (quintet state) and 5 H_2O in aqueous solution - structure *a*

Np	0.0000000	0.0000000	−2.6796416
O	0.0000000	1.8016458	−2.6717745
O	0.0000000	−1.8016458	−2.6717745
Np	0.0000000	0.0000000	1.5674723
O	0.0000000	0.0000000	−0.3061474
O	0.0000000	0.0000000	3.3701188
H	−2.9991935	0.7735312	1.7933538
H	−2.9991935	−0.7735312	1.7933538
O	−2.4762568	0.0000000	1.5102427
H	2.9991935	0.7735312	1.7933538
H	2.9991935	−0.7735312	1.7933538
O	2.4762568	0.0000000	1.5102427
H	0.7739045	−3.0610559	1.7143785
H	−0.7739045	−3.0610559	1.7143785
O	0.0000000	−2.5072836	1.5031665
H	0.7739045	3.0610559	1.7143785
H	−0.7739045	3.0610559	1.7143785
O	0.0000000	2.5072836	1.5031665
O	0.0000000	0.0000000	−5.1673302
H	0.7806627	0.0000000	−5.7493353
H	−0.7806627	0.0000000	−5.7493353

S1.5 T-shaped $[NpO_2]_2^{2+}$ (quintet state) and 5 H_2O in aqueous solution - structure *b*

Np	0.0000000	0.0000000	−2.6130182
O	0.0000000	1.8098420	−2.6169631
O	0.0000000	−1.8098420	−2.6169631
Np	0.0000000	0.0000000	1.6405488
O	0.0000000	0.0000000	−0.2191497
O	0.0000000	0.0000000	3.4371858
H	−2.9657146	0.7806144	−3.2879440
H	−2.9657146	−0.7806144	−3.2879440
O	−2.4021479	0.0000000	−3.1395163
H	2.9657146	0.7806144	−3.2879440
H	2.9657146	−0.7806144	−3.2879440
O	2.4021479	0.0000000	−3.1395163
H	0.7753306	−2.9979750	1.9787369
H	−0.7753306	−2.9979750	1.9787369
O	0.0000000	−2.5090895	1.6449324
H	0.7753306	2.9979750	1.9787369
H	−0.7753306	2.9979750	1.9787369
O	0.0000000	2.5090895	1.6449324
O	0.0000000	0.0000000	−5.1185269
H	0.7803683	0.0000000	−5.6998580
H	−0.7803683	0.0000000	−5.6998580

S1.6 Diamond-shaped $[NpO_2]_2^{2+}$ (quintet state) in aqueous solution

O	−1.6465897	2.7868271	0.0000000
Np	−1.3609598	1.0396809	0.0000000
O	−1.0045405	−0.7859830	0.0000000
O	1.0045405	0.7859830	0.0000000
Np	1.3609598	−1.0396809	0.0000000
O	1.6465897	−2.7868271	0.0000000

S1.7 Diamond-shaped $[NpO_2]_2^{2+}$ and 4 H_2O (quintet state) in aqueous solution

O	−2.4637543	2.1664620	0.0000000
Np	−1.5917139	0.5994842	0.0000000
O	−0.6925893	−1.0703668	0.0000000
O	0.6925893	1.0703668	0.0000000
Np	1.5917139	−0.5994842	0.0000000
O	2.4637543	−2.1664620	0.0000000
O	−1.1420705	0.9515355	2.4012849
H	−1.7803988	1.4889370	2.9084446
H	−0.2628685	1.2321301	2.7204852
O	1.1420705	−0.9515355	−2.4012849
H	1.7803988	−1.4889370	−2.9084446
H	0.2628685	−1.2321301	−2.7204852
O	−1.1420705	0.9515355	−2.4012849
H	−1.7803988	1.4889370	−2.9084446
H	−0.2628685	1.2321301	−2.7204852
O	1.1420705	−0.9515355	2.4012849
H	1.7803988	−1.4889370	2.9084446
H	0.2628685	−1.2321301	2.7204852

S1.8 Diamond-shaped $[NpO_2]_2^{2+}$ and 6 H_2O (quintet state) in aqueous solution

O	−1.6507979	2.8271489	0.0000000
Np	−1.3436518	1.0507846	0.0000000
O	−1.0121053	−0.8155510	0.0000000
O	1.0121053	0.8155510	0.0000000
Np	1.3436518	−1.0507846	0.0000000
O	1.6507979	−2.8271489	0.0000000
O	−3.7312367	0.6720626	0.0000000
H	−4.1996821	−0.1828836	0.0000000
H	−4.4150429	1.3665278	0.0000000
O	3.7312367	−0.6720626	0.0000000
H	4.1996821	0.1828836	0.0000000
H	4.4150429	−1.3665278	0.0000000
O	−1.3175477	1.0038314	2.4998078
H	−2.1299137	1.2560596	2.9782802
H	−0.5922022	1.4222398	3.0000718
O	1.3175477	−1.0038314	−2.4998078
H	2.1299137	−1.2560596	−2.9782802
H	0.5922022	−1.4222398	−3.0000718
O	−1.3175477	1.0038314	−2.4998078
H	−2.1299137	1.2560596	−2.9782802
H	−0.5922022	1.4222398	−3.0000718
O	1.3175477	−1.0038314	2.4998078
H	2.1299137	−1.2560596	2.9782802
H	0.5922022	−1.4222398	3.0000718

S1.9 Diamond-shaped $[NpO_2]_2^{3+}$ (quartet state) in aqueous solution

O	−1.6918911	2.7775097	0.0000000
Np	−1.3770337	1.0711855	0.0000000
O	−1.0486077	−0.7071791	0.0000000
O	1.0486077	0.7071791	0.0000000
Np	1.3770337	−1.0711855	0.0000000
O	1.6918911	−2.7775097	0.0000000

S1.10 Diamond-shaped $[NpO_2]_2^{3+}$ and 4 H_2O (quartet state) in aqueous solution

O	−2.4266595	2.1743207	0.0000000
Np	−1.5914884	0.6280667	0.0000000
O	−0.7197490	−1.0182116	0.0000000
O	0.7197490	1.0182116	0.0000000
Np	1.5914884	−0.6280667	0.0000000
O	2.4266595	−2.1743207	0.0000000
O	−1.1114694	0.9821589	2.3182527
H	−1.8042702	1.4006100	2.8684730
H	−0.2630250	1.3281008	2.6607233
O	1.1114694	−0.9821589	−2.3182527
H	1.8042702	−1.4006100	−2.8684730
H	0.2630250	−1.3281008	−2.6607233
O	−1.1114694	0.9821589	−2.3182527
H	−1.8042702	1.4006100	−2.8684730
H	−0.2630250	1.3281008	−2.6607233
O	1.1114694	−0.9821589	2.3182527
H	1.8042702	−1.4006100	2.8684730
H	0.2630250	−1.3281008	2.6607233

S1.11 Diamond-shaped $[NpO_2]_2^{3+}$ and 6 H_2O (quartet state) in aqueous solution

O	−1.4930851	2.8689464	0.0000000
Np	−1.3302824	1.1078009	0.0000000
O	−1.0689746	−0.7234667	0.0000000
O	1.0689746	0.7234667	0.0000000
Np	1.3302824	−1.1078009	0.0000000
O	1.4930851	−2.8689464	0.0000000
O	−3.6692460	0.9124607	0.0000000
H	−4.1799378	0.0797127	0.0000000
H	−4.3132403	1.6463934	0.0000000
O	3.6692460	−0.9124607	0.0000000
H	4.1799378	−0.0797127	0.0000000
H	4.3132403	−1.6463934	0.0000000
O	−1.2892727	1.1475506	2.3745029
H	−1.4954957	0.4048886	2.9732642
H	−1.3342657	1.9612567	2.9138391
O	1.2892727	−1.1475506	−2.3745029
H	1.4954957	−0.4048886	−2.9732642
H	1.3342657	−1.9612567	−2.9138391
O	−1.2892727	1.1475506	−2.3745029
H	−1.4954957	0.4048886	−2.9732642
H	−1.3342657	1.9612567	−2.9138391
O	1.2892727	−1.1475506	2.3745029
H	1.4954957	−0.4048886	2.9732642
H	1.3342657	−1.9612567	2.9138391

S2 Bond lengths and angles

Figure S1: The geometries of CCIs with explicit first coordination sphere. T-shaped clusters are characterized by C_{2v} symmetry and diamond-shaped molecules are featured by C_{2h} symmetry if not mentioned otherwise. The figure shows (a) and (b) the T-shaped molecule with five water molecules – two different configurations, (c) the T-shaped molecule with three water molecules, (d) the T-shaped molecule with four water molecules, (e) the diamond-shaped molecule with four water molecules, (f) the diamond-shaped molecule with six water molecules, (g) and (h) the T-shaped molecule with nine water molecules – two different configurations with symmetry C_s, (i) the diamond-shaped molecule with eight water molecules, and (j) the diamond-shaped molecule with eight water molecules – symmetry C_i,

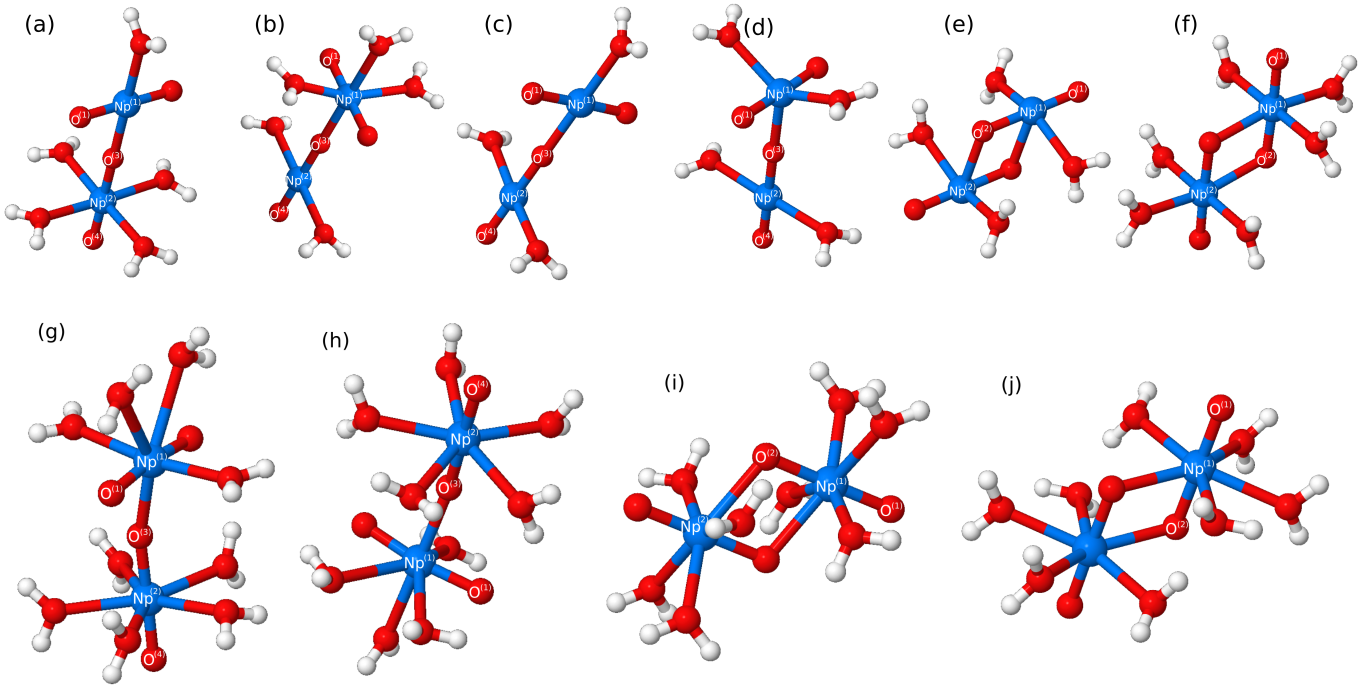


Figure S2: BP86 optimized bond lengths [Å] of the T-shaped $[NpO_2]_2^{2+}$ in different environments. The environment is given in parentheses, where "v" indicates vacuum, while "s" corresponds to aqueous solution. M denotes the spin multiplicity. The $Np^{(1)}$–$O^{(1)}$ bond length equals $Np^{(1)}$–$O^{(2)}$.

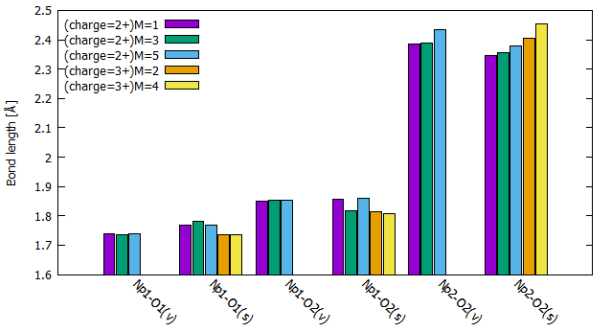
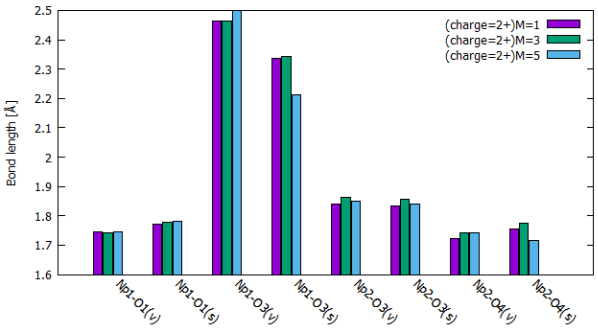


Figure S3: BP86 optimized bond lengths [Å] of the diamond-shaped $[NpO_2]_2^{2+}$ and $[NpO_2]_2^{3+}$ in different environments. The environment is given in parentheses, where "v" indicates vacuum, while "s" corresponds to aqueous solution. M denotes the spin multiplicity. The bond lengths $Np^{(1)}$–$O^{(1)}$ and $Np^{(1)}$–$O^{(2)}$ equal $Np^{(2)}$–$O^{(4)}$ and $Np^{(2)}$–$O^{(3)}$, respectively.



S2.1 T-shaped $[NpO_2]_2^{2+}$

Table S1: BP86 optimized structural parameters (bond lengths [Å] and angles [°]) of the T-shaped $[NpO_2]_2^{2+}$ and $[NpO_2]_2^{3+}$ in different environments. M denotes the spin multiplicity. The column "H_2O" indicates the number of explicit water molecules in a given system. Index "p" encodes that water molecules are perpendicular to the dineptunyl molecule. ∠ symbolises the angle between $Np^{(1)}$, $O^{(1)}$, and $O^{(3)}$. The bond length $O^{(1)}$–$Np^{(1)}$ is equal to $O^{(2)}$–$Np^{(1)}$.

		H_2O	$O^{(1)}$-$Np^{(1)}$	$Np^{(1)}$-$O^{(3)}$	$O^{(3)}$-$Np^{(2)}$	$Np^{(2)}$-$O^{(4)}$	∠	$Np^{(1)}$-H_2O	$Np^{(2)}$-H_2O	$Np^{(1)}$-$Np^{(2)}$
Vacuum	$[(NpO_2)_2]^{2+}_{[M=1]}$	–	1.744	2.465	1.839	1.724	90	–	–	4.304
	$[(NpO_2)_2]^{2+}_{[M=3]}$	–	1.741	2.465	1.862	1.742	90	–	–	4.328
	$[(NpO_2)_2]^{2+}_{[M=5]}$	–	1.747	2.500	1.851	1.741	90	–	–	4.351
Solution	$[(NpO_2)_2]^{2+}_{[M=1]}$	–	1.772	2.338	1.834	1.756	91	–	–	4.172
	$[(NpO_2)_2]^{2+}_{[M=3]}$	–	1.778	2.344	1.856	1.775	90	–	–	4.200
	$[(NpO_2)_2]^{2+}_{[M=5]}$	–	1.781	2.211	1.841	1.717	90	–	–	4.052
	$[(NpO_2)_2]^{2+}_{[M=5]}$	2	1.791	2.348	1.864	1.787	90	–	2.430	4.211
	$[(NpO_2)_2]^{2+}_{[M=5]}$	3	1.800	2.401	1.853	1.788	89	2.445	2.476	4.254
	$[(NpO_2)_2]^{2+}_{[M=5]}$	4	1.802	2.367	1.869	1.794	91	2.418	2.462	4.236
	$[(NpO_2)_2]^{2+}_{[M=5],a}$	5	1.802	2.373	1.874	1.803	90	2.488	$2.508/2.480^p$	4.247
	$[(NpO_2)_2]^{2+}_{[M=5],b}$	5	1.810	2.394	1.860	1.797	90	$2.506/2.459^p$	2.509	4.254
	$[(NpO_2)_2]^{2+}_{[M=5]}$	7	1.799	2.300	1.901	1.812	91	$2.521/2.419^p$	$2.515/2.510^p$	4.201
	$[(NpO_2)_2]^{2+}_{[M=5]}$	9	1.827	2.392	1.868	1.813	86	2.848/2.477	2.500/2.510	4.220
	$[(NpO_2)_2]^{2+}_{[M=5]}$	9	1.832	2.390	1.872	1.811	89	2.469–2.776	2.505–2.541	4.209

The addition of explicit water molecules to the cation-cation neptunyl complex elongates (up to 0.2

Å) the CCI bond length, which is the bridge between two neptunyl units. The other Np–O distances increase slightly and the corresponding differences amount to 0.1 Å (less than 6% of the total bond length). The angle between the two monomers changes marginally (up to 4°).

S2.2 Diamond-shaped $[NpO_2]_2^{2+}$ and $[NpO_2]_2^{3+}$

Table S2: BP86 optimized structural parameters (bond lengths [Å] and angles [°]) of the diamond-shaped $[NpO_2]_2^{2+}$ and $[NpO_2]_2^{3+}$ in different environments. M denotes the spin multiplicity. The column "H_2O" indicates the number of explicit water molecules in a given system. The index "p" encodes the water molecules are perpendicular to the dineptunyl molecule. $\angle_1$ denotes the angle between $O^{(1)}$, $Np^{(1)}$, and $O^{(3)}$, while $\angle_2$ stands for the angle between $O^{(1)}$, $Np^{(1)}$, and $O^{(2)}$. The bond lengths $O^{(1)}$–$Np^{(1)}$ and $Np^{(1)}$–$O^{(2)}$ are symmetric to $O^{(4)}$–$Np^{(2)}$ and $Np^{(2)}$–$O^{(3)}$, respectively.

		H_2O	$O^{(1)}$-$Np^{(1)}$	$Np^{(1)}$-$O^{(2)}$	$Np^{(1)}$-$O^{(3)}$	$\angle_1$	$\angle_2$	$Np^{(1)}$-H_2O^p	$Np^{(1)}$-H_2O	$Np^{(1)}$-$Np^{(2)}$
Vacuum	$[(NpO_2)_2]^{2+}_{[M=1]}$	–	1.738	1.851	2.386	107	179	–	–	3.429
	$[(NpO_2)_2]^{2+}_{[M=3]}$	–	1.737	1.854	2.390	108	180	–	–	3.449
	$[(NpO_2)_2]^{2+}_{[M=5]}$	–	1.739	1.852	2.433	109	183	–	–	3.509
Solution	$[(NpO_2)_2]^{2+}_{[M=1]}$	–	1.768	1.858	2.346	105	179	–	–	3.357
	$[(NpO_2)_2]^{2+}_{[M=3]}$	–	1.780	1.818	2.357	106	182	–	–	3.450
	$[(NpO_2)_2]^{2+}_{[M=5]}$	–	1.770	1.860	2.379	107	182	–	–	3.425
	$[(NpO_2)_2]^{2+}_{[M=5]}$	4	1.783	1.897	2.332	107	181	2.468	–	3.402
	$[(NpO_2)_2]^{2+}_{[M=5]}$	6	1.803	1.896	2.367	106	180	2.417	2.500	3.411
	$[(NpO_2)_2]^{2+}_{[M=5]}$	8	1.813	1.883	2.497	108	180	2.494	2.529	3.551
	$[(NpO_2)_2]^{2+}_{[C_i,M=5]}$	8	1.811	1.880	2.476	107	179	2.478	2.489	3.519
	$[(NpO_2)_2]^{3+}_{[M=2]}$	–	1.734	1.815	2.406	109	180	–	–	–
	$[(NpO_2)_2]^{3+}_{[M=4]}$	–	1.735	1.808	2.453	109	180	–	–	3.489
	$[(NpO_2)_2]^{3+}_{[M=4]}$	4	1.757	1.863	2.349	109	180	2.394	–	3.431
	$[(NpO_2)_2]^{3+}_{[M=4]}$	6	1.769	1.850	2.430	104	183	2.347	2.375	3.462
	$[(NpO_2)_2]^{3+}_{[M=4]}$	8	1.775	1.840	2.503	108	177	2.478	2.415	3.542
	$[(NpO_2)_2]^{3+}_{[C_i,M=4]}$	8	1.772	1.828	2.609	111	178	2.393	2.442	3.637

In $[(NpO_2)_2]^{2+}_{[M=5]}$, all Np–O bonds are almost unaffected by explicitly including the first coordination sphere as the differences in bond lengths amount to 0.05 Å, which is less than 3% of a total bond length. We observe that the ligated water molecules slightly reduce the bending in the monomers. In $[(NpO_2)_2]^{3+}_{[M=4]}$, the "yl" bond distances are elongated up to 0.1 Å. One pronounced feature is that the number of water molecules influences the CCI bond length, which elongates in the complex with eight water molecules. The linearity of the monomers is slightly distorted (up to 5°) in the compound with eight surrounding water molecules in the first coordination sphere.

S2.3 Crystalline structures

Table S3: Np–O bond lengths in some new crystalline structures. The ranges are for structures, where more than one bond of a given type occurs.

	Np – O_{yl} [Å]	Np – $O_{bridging}$ [Å]	
$Na_4[(NpO_2)_2C_6(COO)_6] \cdot 8\ H_2O$	1.85 – 1.91	2.360 – 2.479	[1]
$(NH_4)_3[(NpO_2)_5(C_6H_2(COO)_4)_2] \cdot 7\ H_2O$	1.832 – 1.876	2.373 – 2.481	[2]
$[(NpO_2(salen))_4(\mu_8\text{-}K)_2][K(18C6)Py]_2$	1.832 – 1.881	2.512	[3]
$(NpO_2)_2(SeO_4)(H_2O)_4$	1.834 – 1.852	2.395 – 2.545	[4]
$(NpO_2)_3(OH)(SeO_3)(H_2O)_2 \cdot H_2O$	1.855 – 1.880	2.314 – 2.595	[5]
$Na(NpO_2)(SeO_3)(H_2O)$	1.82 – 1.829	2.30 – 2.531	[5]
$NpO_2(B_8O_{11}(OH)_4)$	1.737 – 1.746	2.399 – 2.639	[6]
$K_{11}(NpO_2)_{23}(OOCC_6H_5)_{57}(H_2O)_{18+x}$	1.700 – 1.766	2.322 – 2.593	[7]

S3 DFT energetics

Table S4: Relative energies of the CCIs. DFT single-point calculations were performed for (1) the bare neptunyl(V)-neptunyl(V) clusters with geometries optimized without an explicit first coordination sphere (index in parentheses corresponds to the index in Figure S1), (2) neptunyl dimers with complete explicit first coordination sphere, and (3) the neptunyl dimers with four water molecules. The COSMO model was used in all DFT calculations.

			ΔE [kcal/mol]						
	Shape		H_2O	BP86	PBE0	PBE0-D3	B3LYP	B3LYP-D3	CASPT2/SO-RASSI*
(1)	T-shaped	$[(NpO_2)_2]^{2+}_{[(i),M=5]}$	–	6	9	8	8	7	10
	D-shaped	$[(NpO_2)_2]^{2+}_{[(j),M=5]}$	–	0	0	0	0	0	0
(2)	D-shaped	$[(NpO_2)_2]^{2+}_{[(i),M=5]}$	8	9	7	7	7	7	
	D-shaped	$[(NpO_2)_2]^{2+}_{[(j),M=5]}$	8	0	0	0	0	0	
	D-shaped	$[(NpO_2)_2]^{3+}_{[(i),M=4]}$	8	5	4	5	4	6	
	D-shaped	$[(NpO_2)_2]^{3+}_{[(j),M=4]}$	8	0	0	0	0	0	
	T-shaped	$[(NpO_2)_2]^{2+}_{[(g),M=5]}$	9	0	0	0	0	0	
	T-shaped	$[(NpO_2)_2]^{2+}_{[(h),M=5]}$	9	1	1	0	1	0	
(3)	T-shaped	$[(NpO_2)_2]^{2+}_{[M=5]}$	4	9	0	0	0	0	
	D-shaped	$[(NpO_2)_2]^{2+}_{[M=5]}$	4	0	20	17	15	11	

S4 Bader population analysis

A bond energy analysis [8–10] and a Bader population analysis [11, 12] has been performed with the ADF2014 software suite [13–15] using a TZP basis [16] for all atoms. In all calculations, scalar relativistic effects (ZORA Hamiltonian [17–19]) and solvation effects (COSMO solvation model [20]) have been included. This analysis has been performed for $[NpO_2]_2^{2+}$ (quintet state) in both structural rearrangements and for the diamond-shaped $[NpO_2]_2^{3+}$ (quartet state) with and without an explicit first coordination shell. The molecular geometries were taken from calculations with an explicit first coordination shell as they are closer to experimental values.

Table S5 presents the Bader analysis of the fully hydrated molecule compared to the implicit solvation model. The positive charge is focused on the Np centers, but the explicit water molecules slightly decrease it, which is balanced by the small rise of the negative charge on the O atoms. The T-shaped conformation possesses a dipole moment with a value of −129 a.u. in the direction determined by the ($O^{(3)}$–$Np^{(2)}$–$O^{(4)}$) unit.

The Bader population analysis for the diamond-shaped molecules with and without an explicit first coordination shell is presented in Tab S5. The positive charge on the actinide centers is reduced if water molecules are included explicitly in the solvation model. The O atoms that interact with the Np atom of the other monomer are characterized by more negative charge in contrast to the external oxygen atoms. The changes in spin densities centered on the atoms are rather minor for both solvation models.

Table S5: Bader population analysis for the investigated structures (optimized for PBE0 functional combined with ZORA Hamiltonian and with the COSMO solvation model), where M stands for the multiplicity. The charge and population of the $O^{(2)}$ atom is exactly the same as for $O^{(1)}$ in T-shaped structure or the same as for $O^{(3)}$ in diamond-shaped structures. We compare the structures with and without explicit first coordination shell.

		T-shaped cluster		Diamond-shaped cluster			
		$[(NpO_2)_2]^{2+}_{[M=5]}$		$[(NpO_2)_2]^{2+}_{[M=5]}$		$[(NpO_2)_2]^{3+}_{[M=4]}$	
			$+9H_2O$		$+8H_2O$		$+8H_2O$
$Np^{(1)}$	charge	2.80	2.69	2.88	2.70	3.06	2.82
	spin density	2.19	2.16	2.20	2.17	1.69	1.66
$Np^{(2)}$	charge	2.93	2.70	2.88	2.70	3.06	2.82
	spin density	2.23	2.18	2.20	2.17	1.69	1.66
$O^{(1)}$	charge	-0.96	-1.00	-0.88	-0.96	-0.71	-0.81
	spin density	-0.10	-0.09	-0.12	-0.10	-0.11	-0.08
$O^{(3)}$	charge	-0.98	-1.05	-1.00	-1.05	-0.85	-0.92
	spin density	-0.10	-0.07	-0.08	-0.07	-0.08	-0.07
$O^{(4)}$	charge	-0.85	-0.95	-1.00	-1.05	-0.85	-0.92
	spin density	-0.13	-0.10	-0.08	-0.07	-0.08	-0.07

S5 Energy decompostion analysis

Table S6: Energy decomposition analysis [8–10] performed with the ADF 2014 program. [13–15] We used the UKS-DFT method with the hybrid PBE0 exchange–correlation functional, the ZORA scalar relativistic Hamiltonian, [17–19] and the COSMO solvation model. [**?**, **?**, 20] The TZP basis set was used for all atoms. [16] The interaction energies consist of the Pauli repulsion energies, electronstatic interactions energies, and orbital interactions energies. The interaction energies indicate similar trends as binding energy analysis presented in Table 10 of the manuscript.

	T-shaped $[NpO_2]_2^{2+}$ + 9 H_2O [kcal/mol]	Diamond-shaped $[NpO_2]_2^{2+}$ + 8 H_2O [kcal/mol]	Diamond-shaped $[NpO_2]_2^{3+}$ + 8 H_2O [kcal/mol]
Pauli repulsion	46	115	75
Electrostatic interactions	-14	-71	29
Orbital Interactions	-27	-55	-50
Solvation Energy	-188	-198	-375
Total bonding energy	-181	-207	-319
Interaction energy	5	-11	54
	T-shaped $[NpO_2]_2^{2+}$ [kcal/mol]	Diamond-shaped $[NpO_2]_2^{2+}$ [kcal/mol]	Diamond-shaped $[NpO_2]_2^{3+}$ [kcal/mol]
Pauli repulsion	40	82	46
Electrostatic interactions	24	-11	117
Orbital Interactions	-23	-53	-70
Solvation Energy	-333	-322	-589
Total bonding energy	-290	-303	-495
Interaction energy	42	18	94
	T-shaped $[NpO_2]_2^{2+}$ + 4 H_2O [kcal/mol]	Diamond-shaped $[NpO_2]_2^{2+}$ + 4 H_2O [kcal/mol]	
Pauli repulsion	46	151	
Electrostatic interactions	-4	-85	
Orbital Interactions	-22	-69	
Solvation Energy	-247	-236	
Total bonding energy	-225	-238	
Interaction energy	20	-3	

S6 Vibrational spectra

Table S7: Vibrational spectra of T-shaped $[NpO_2]_2^{2+}$ computed using DFT with the BP86 exchange–correlation functional. M denotes spin multiplicity. Solution effects were included using the COSMO model.

		Compound	Symmetry	Wave number cm^{-1}	IR intensity km/mol	Selection rules IR	RAMAN
T-shaped clusters	Vacuum	$[(NpO_2)_2]^{2+}_{[M=1]}$	a_1	965	210	yes	yes
			b_1	994	226	yes	yes
		$[(NpO_2)_2]^{2+}_{[M=3]}$	b_1	995	226	yes	yes
		$[(NpO_2)_2]^{2+}_{[M=5]}$	a_1	947	203	yes	yes
			b_1	984	228	yes	yes
	Solution	$[(NpO_2)_2]^{2+}_{[M=1]}$	a_1	753	767	yes	yes
			a_1	869	636	yes	yes
			b_1	896	966	yes	yes
		$[(NpO_2)_2]^{2+}_{[M=5]}$	a_1	803	577	yes	yes
			a_1	864	613	yes	yes
			b_1	877	705	yes	yes
Diamond-shaped clusters	Vacuum	$[(NpO_2)_2]^{2+}_{[M=1]}$	b_u	953	345	yes	no
		$[(NpO_2)_2]^{2+}_{[M=3]}$	b_u	953	330	yes	no
		$[(NpO_2)_2]^{2+}_{[M=5]}$	b_u	774	219	yes	no
			b_u	948	368	yes	no
	Solution	$[(NpO_2)_2]^{2+}_{[M=5]}$	b_u	342	229	yes	no
			b_u	735	543	yes	no
			b_u	854	1041	yes	no
		$[(NpO_2)_2]^{3+}_{[M=2]}$	b_u	939	881	yes	no
		$[(NpO_2)_2]^{3+}_{[M=4]}$	b_u	932	960	yes	no

S7 CASSCF+ECP active space orbitals

Please note, that not all orbitals can be clearly named with $D_{\infty h}$ labels as single neptunyl orbitals of different symmetry mix, in particular in the virtual orbital space. The mixed orbitals, which are composed of σ_g^*, π_g^*, and π_u^* orbitals, are:

- in the T-shaped $[NpO_2]_2^{2+}$ cluster: $10a_1$, $13a_1$, $14a_1$, $15a_1$, $16a_1$, $7b_1$, $8b_1$, $6b_2$, $7b_2$, and $8b_2$,

- in the diamond-shaped $[NpO_2]_2^{2+}$ molecule: $9a_g$, $7a_u$, $8a_u$, $9a_u$, $10b_u$, $11b_u$, $12b_u$, $7b_g$, $8b_g$, and $9b_g$,

- in the diamond-shaped $[NpO_2]_2^{3+}$ complex: $10a_g$, $11a_g$, $13a_g$, $14a_g$, $7a_u$, $8a_u$, $9a_u$, $10b_u$, $12b_u$, $13b_u$, $14b_u$, $6b_g$, $7b_g$, $8b_g$, and $9b_g$.

Table S8: C_{2v} and C_{2h} labels and corresponding $D_{\infty h}$ labels of linear neptunyls.

	T-shaped clusters (C_{2v})	Diamond-shaped clusters (C_{2h})	
$D_{\infty h}$ labels	$[NpO_2]_2^{2+}$	$[NpO_2]_2^{2+}$	$[NpO_2]_2^{3+}$
σ_g	$2a_1$ $3a_1$ $4a_1$	$5a_g$ $5b_u$	$5a_g$ $5b_u$
σ_g^*	$12a_1$ $11a_1$ $4b_1$	$8a_g$ $8b_u$	$8a_g$ $8b_u$
π_g	$2b_2$ $5a_1$ $2b_1$ $1b_2$	$4a_g$ $3a_u$ $2b_u$ $3b_u$ $3b_g$	$4a_g$ $3a_u$ $9a_u$ $9b_g$
π_g^*	$10b_2$	$11a_g$	
π_u	$9a_1$ $11b_2$ $10b_1$ $3b_1$ $1b_1$ $3a_2$	$2a_g$ $2a_u$ $6a_u$ $2b_g$	$2a_g$ $2a_u$ $6a_u$ $3b_u$ $2b_g$
π_u^*	$9b_1$ $4a_2$		
δ_u	$6a_1$ $5b_1$ $1a_2$ $2a_2$	$6a_g$ $4a_u$ $6b_u$ $4b_g$	$7a_g$ $5a_u$ $7b_u$ $5b_g$
ϕ_u	$7a_1$ $6b_1$ $3b_2$ $4b_2$	$7a_g$ $5a_u$ $7b_u$ $5b_g$	$6a_g$ $4a_u$ $6b_u$ $4b_g$

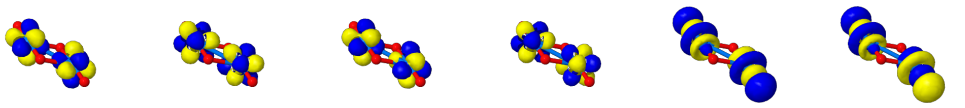
S7.1 T-shaped $[NpO_2]_2^{2+}$

Figure S4: The CASSCF natural orbitals for the quintet state of the T-shaped $[NpO_2]_2^{2+}$. The corresponding natural occupation numbers are given in parentheses.

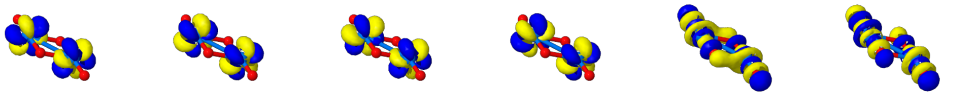
$2a_1$ (0.43) $2b_1$ (0.46) $1b_2$ (0.46) $2b_2$ (0.44) $1a_1$ (0.54) $1b_1$ (0.56) $1a_2$ (0.57) $2a_2$ (0.54)

S7.2 Diamond-shaped $[NpO_2]_2^{2+}$

Figure S5: The CASSCF natural orbitals for the quintet state of the diamond-shaped $[NpO_2]_2^{2+}$. The corresponding natural occupation numbers are given in parentheses.



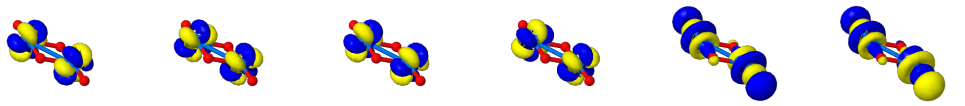
$2a_g$ (0.52) $1a_u$ (0.55) $2b_u$ (0.52) $1b_g$ (0.50) $1a_g$ (1.93) $1b_u$ (1.93)



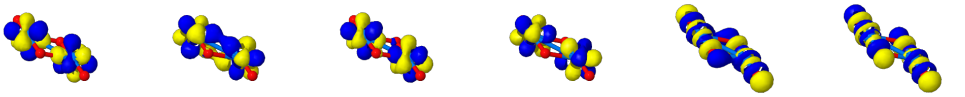
$3a_g$ (0.46) $2a_u$ (0.47) $3b_u$ (0.46) $2b_g$ (0.47) $4a_g$ (0.07) $4b_u$ (0.07)

S7.3 Diamond-shaped $[NpO_2]_2^{3+}$

Figure S6: The CASSCF natural orbitals for the quintet state of the diamond-shaped $[NpO_2]_2^{3+}$. The corresponding natural occupation numbers are given in parentheses.



$2a_g$ (0.51) $1a_u$ (0.50) $2b_u$ (0.51) $1b_g$ (0.55) $1a_g$ (1.93) $1b_u$ (1.93)



$3a_g$ (0.26) $2a_u$ (0.29) $3b_u$ (0.21) $2b_g$ (0.24) $4a_g$ (0.07) $4b_u$ (0.07)

S8 CASSCF+ECP wavefunctions

Table S9: Energetics of the diamond-shaped $[NpO_2]_2^{2+}$, diamond-shaped $[NpO_2]_2^{3+}$, and T-shaped $[NpO_2]_2^{2+}$ molecules. For each molecule, the energy differences are calculated with respect to the lowest lying symmetry state.

Diamond-shaped $[NpO_2]_2^{2+}$		Diamond-shaped $[NpO_2]_2^{3+}$		T-shaped $[NpO_2]_2^{2+}$	
State	Energy [mE_h]	State	Energy [mE_h]	State	Energy [mE_h]
1^5A_g	0.000	1^4A_g	2.583	1^5A_1	0.000
2^5A_g	0.023	2^4A_g	6.696	2^5A_1	15.837
1^5A_u	0.005	1^4A_u	3.524	1^5B_1	0.006
2^5A_u	15.867	2^4A_u	6.692	2^5B_1	32.438
1^5B_u	15.848	1^4B_u	0.000	1^5B_2	0.006
2^5B_u	34.335	2^4B_u	3.540	2^5B_2	16.606
1^5B_g	0.018	1^4B_g	0.002	1^5A_2	0.000
2^5B_g	15.856	2^4B_g	2.595	2^5A_2	15.837

S8.1 Most important determinants in T-shaped $[NpO_2]_2^{2+}$.

Table S10: Most important determinants in wave function of the T-shaped $[NpO_2]_2^{2+}$, their weights and occupation of the active space orbitals.

		Orbital occupation							
State	**Weight**	**1a$_1$**	**2a$_1$**	**1b$_1$**	**2b$_1$**	**1b$_2$**	**2b$_2$**	**1a$_2$**	**2a$_2$**
1^5A_1	0.51	0	0	0	0	1_α	1_α	1_α	1_α
	0.51	1_α	0	0	1_α	0	1_α	1_α	0
	-0.49	1_α	1_α	1_α	1_α	0	0	0	0
	-0.39	0	1_α	1_α	0	1_α	0	0	1_α
2^5A_1	0.58	0	0	1_α	1_α	0	0	1_α	1_α
	-0.58	1_α	0	1_α	0	1_α	0	1_α	0
	0.40	1_α	1_α	0	0	1_α	1_α	0	0
	-0.40	0	1_α	0	1_α	0	1_α	0	1_α
1^5B_1	0.50	1_α	0	1_α	0	1_α	1_α	0	0
	-0.50	0	0	1_α	1_α	0	1_α	0	1_α
	0.50	0	1_α	0	1_α	0	0	1_α	1_α
	-0.50	1_α	1_α	0	0	1_α	0	1_α	0
2^5B_1	0.67	1_α	0	1_α	0	0	0	1_α	1_α
	-0.48	0	0	1_α	1_α	1_α	0	1_α	0
	-0.46	1_α	1_α	0	0	0	1_α	0	1_α
	0.33	0	1_α	0	1_α	1_α	1_α	0	0
1^5B_2	0.50	1_α	0	1_α	1_α	0	1_α	0	0
	0.50	0	0	1_α	0	1_α	1_α	0	1_α
	-0.50	0	1_α	0	0	1_α	0	1_α	1_α
	-0.50	1_α	1_α	0	1_α	0	0	1_α	0
2^5B_2	0.58	1_α	0	0	0	0	1_α	1_α	1_α
	-0.56	1_α	1_α	1_α	0	0	0	0	1_α
	-0.42	0	0	0	1_α	1_α	1_α	1_α	0
	0.40	0	1_α	1_α	1_α	1_α	0	0	0
1^5A_2	0.50	0	0	0	1_α	0	1_α	1_α	1_α
	-0.50	1_α	0	0	0	1_α	1_α	1_α	0
	0.50	1_α	1_α	1_α	0	1_α	0	0	0
	-0.50	0	1_α	1_α	1_α	0	0	0	1_α
2^5A_2	0.57	0	0	1_α	0	1_α	0	1_α	1_α
	-0.50	1_α	0	1_α	1_α	0	0	1_α	0
	-0.40	1_α	1_α	0	1_α	0	1_α	0	0
	0.40	0	1_α	0	0	1_α	1_α	0	1_α

S8.2 Most important determinants in diamond-shaped $[NpO_2]_2^{2+}$.

Table S11: Components of the $[NpO_2]_2^{2+}$ wave functions.

		Orbital occupation										
State	**Weight**	**1a$_g$**	**2a$_g$**	**3a$_g$**	**4a$_g$**	**1a$_u$**	**2a$_u$**	**1b$_u$**	**2b$_u$**	**3b$_u$**	**4b$_u$**	**1b$_g$**	**2b$_g$**
1^5A_g	-0.45	2	0	1_α	0	1_α	0	2	0	1_α	0	1_α	0
	-0.43	2	1_α	0	0	0	1_α	2	1_α	0	0	0	1_α
	-0.30	2	0	0	0	1_α	1_α	2	1_α	1_α	0	0	0
	-0.30	2	1_α	1_α	0	0	0	2	0	0	0	1_α	1_α
2^5A_g	0.48	2	0	0	0	1_α	1_α	2	0	0	0	1_α	1_α
	-0.43	2	1_α	1_α	0	0	0	2	1_α	1_α	0	0	0
	0.31	2	1_α	1_α	0	1_α	1_α	2	0	0	0	0	0
	0.30	2	1_α	0	0	1_α	0	2	0	1_α	0	0	1_α
1^5A_u	0.35	2	0	1_α	0	1_α	0	2	0	0	0	1_α	1_α
	0.35	2	0	0	0	1_α	1_α	2	0	1_α	0	1_α	0
	-0.34	2	0	0	0	1_α	1_α	2	1_α	0	0	0	1_α
	0.34	2	1_α	0	0	0	1_α	2	0	0	0	1_α	1_α
	-0.33	2	0	1_α	0	1_α	0	2	1_α	1_α	0	0	0
	-0.33	2	1_α	1_α	0	0	0	2	0	1_α	0	1_α	0
	0.32	2	1_α	1_α	0	0	0	2	1_α	0	0	0	1_α
	0.32	2	1_α	0	0	0	1_α	2	1_α	1_α	0	0	0
2^5A_u	0.40	2	1_α	0	0	1_α	0	2	0	0	0	1_α	1_α
	-0.40	2	0	0	0	1_α	1_α	2	1_α	0	0	1_α	0
	-0.38	2	1_α	0	0	1_α	0	2	1_α	1_α	0	0	0
	0.38	2	1_α	1_α	0	0	0	2	1_α	0	0	1_α	0
1^5B_u	0.40	2	1_α	1_α	0	1_α	0	2	0	0	0	1_α	0
	0.39	2	0	0	0	1_α	0	2	1_α	1_α	0	1_α	0
	-0.39	2	1_α	0	0	1_α	1_α	2	1_α	0	0	0	0
	-0.38	2	1_α	0	0	0	0	2	1_α	0	0	1_α	1_α
2^5B_u	0.35	2	1_α	1_α	0	1_α	0	2	0	0	0	0	1_α
	-0.34	2	1_α	0	0	1_α	1_α	2	0	1_α	0	0	0
	-0.34	2	0	1_α	0	1_α	1_α	2	1_α	0	0	0	0
	-0.34	2	0	0	0	1_α	0	2	1_α	1_α	0	0	1_α
	0.34	2	0	1_α	0	0	0	2	1_α	0	0	1_α	1_α
	0.34	2	1_α	1_α	0	0	1_α	2	0	0	0	1_α	0
	-0.34	2	0	0	0	0	1_α	2	1_α	1_α	0	1_α	0
	0.34	2	1_α	0	0	0	0	2	0	1_α	0	1_α	1_α
1^5B_g	0.35	2	0	1_α	0	1_α	1_α	2	0	0	0	1_α	0
	0.35	2	1_α	0	0	1_α	1_α	2	0	0	0	0	1_α
	-0.34	2	0	0	0	1_α	0	2	0	1_α	0	1_α	1_α
	-0.34	2	0	0	0	0	1_α	2	1_α	0	0	1_α	1_α
	-0.33	2	1_α	1_α	0	1_α	0	2	0	1_α	0	0	0
	0.33	2	0	1_α	0	0	0	2	1_α	1_α	0	1_α	0
	0.32	2	1_α	0	0	0	0	2	1_α	1_α	0	0	1_α
	-0.32	2	1_α	1_α	0	0	1_α	2	1_α	0	0	0	0
2^5B_g	0.40	2	1_α	0	0	1_α	1_α	2	0	0	0	1_α	0
	0.40	2	0	0	0	1_α	0	2	1_α	0	0	1_α	1_α
	0.38	2	1_α	1_α	0	1_α	0	2	1_α	0	0	0	0
	0.38	2	1_α	0	0	0	0	2	1_α	1_α	0	1_α	0

S8.3 Most important determinants in diamond-shaped $[NpO_2]_2^{3+}$.

Table S12: Most important determinants in the wave functions of the diamond-shaped $[NpO_2]_2^{3+}$, their weights and occupation of the active space orbitals.

		Orbital occupation											
State	**Weight**	**1a$_g$**	**2a$_g$**	**3a$_g$**	**4a$_g$**	**1a$_u$**	**2a$_u$**	**1b$_u$**	**2b$_u$**	**3b$_u$**	**4b$_u$**	**1b$_g$**	**2b$_g$**
1^4A_g	0.54	2	1_α	0	0	1_α	1_α	2	0	0	0	0	0
	0.53	2	0	0	0	0	1_α	2	1_α	0	0	1_α	0
	0.41	2	0	0	0	1_α	0	2	0	1_α	0	1_α	0
	0.39	2	1_α	0	0	0	0	2	1_α	1_α	0	0	0
2^4A_g	0.50	2	1_α	0	0	0	0	2	1_α	1_α	0	0	0
	-0.49	2	1_α	0	0	0	0	2	0	0	0	1_α	1_α
	0.48	2	0	0	0	1_α	0	2	1_α	0	0	0	1_α
	-0.43	2	0	0	0	1_α	0	2	0	1_α	0	1_α	0
1^4A_u	0.50	2	0	1_α	0	0	0	2	1_α	0	0	1_α	0
	-0.50	2	1_α	1_α	0	1_α	0	2	0	0	0	0	0
	0.47	2	0	0	0	1_α	0	2	0	0	0	1_α	1_α
	-0.40	2	1_α	0	0	0	0	2	1_α	0	0	0	1_α
2^4A_u	0.52	2	1_α	0	0	0	0	2	1_α	0	0	0	1_α
	-0.46	2	0	0	0	1_α	0	2	1_α	1_α	0	0	0
	-0.46	2	1_α	0	0	0	0	2	0	1_α	0	1_α	0
	0.45	2	0	0	0	1_α	0	2	0	0	0	1_α	1_α
1^4B_u	-0.47	2	0	1_α	0	1_α	0	2	0	0	0	1_α	0
	0.50	2	0	0	0	1_α	1_α	2	1_α	0	0	0	0
	-0.49	2	1_α	0	0	0	1_α	2	0	0	0	1_α	0
	0.44	2	1_α	1_α	0	0	0	2	1_α	0	0	0	0
2^4B_u	0.52	2	1_α	1_α	0	0	0	2	1_α	0	0	0	0
	0.49	2	0	1_α	0	1_α	0	2	0	0	0	1_α	0
	-0.44	2	1_α	0	0	1_α	0	2	0	0	0	0	1_α
	-0.44	2	0	0	0	0	0	2	1_α	0	0	1_α	1_α
1^4B_g	0.52	2	0	0	0	1_α	1_α	2	0	0	0	1_α	0
	0.47	2	1_α	0	0	0	1_α	2	1_α	0	0	0	0
	0.46	2	1_α	1_α	0	0	0	2	0	0	0	1_α	0
	0.45	2	0	1_α	0	1_α	0	2	1_α	0	0	0	0
2^4B_g	0.57	2	1_α	0	0	0	1_α	2	1_α	0	0	0	0
	-0.50	2	0	0	0	1_α	1_α	2	0	0	0	1_α	0
	-0.40	2	0	0	0	0	0	2	1_α	1_α	0	1_α	0
	0.40	2	1_α	0	0	1_α	0	2	0	1_α	0	0	0

S9 CASSCF+DKH2 wavefunctions

S9.1 Most important determinants in T-shaped $[NpO_2]_2^{2+}$.

Table S13: Components of the wave function of the T-shaped $[NpO_2]_2^{2+}$ molecule.

		Orbital occupation							
State	**Weight**	**1a$_1$**	**2a$_1$**	**1b$_2$**	**2b$_2$**	**1b$_1$**	**2b$_1$**	**1a$_2$**	**2a$_2$**
1^5A_1	0.49177	1_α	1_α	0	0	1_α	1_α	0	0
	-0.50810	0	0	1_α	1_α	0	0	1_α	1_α
	0.48693	0	1_α	1_α	0	0	1_α	0	1_α
	0.50318	1_α	0	0	1_α	1_α	0	1_α	0
2^5A_1	0.39284	1_α	1_α	1_α	1_α	0	0	0	0
	-0.58226	1_α	0	1_α	0	0	1_α	1_α	0
	0.38898	0	1_α	0	1_α	1_α	0	0	1_α
	0.58794	0	0	0	0	1_α	1_α	1_α	1_α
3^5A_1	0.57365	1_α	1_α	0	0	0	0	1_α	1_α
	0.40922	0	0	1_α	1_α	1_α	1_α	0	0
	0.39689	0	1_α	1_α	0	1_α	0	1_α	0
	-0.57978	1_α	0	0	1_α	0	1_α	0	1_α
4^5A_1	0.50808	1_α	1_α	0	0	1_α	1_α	0	0
	0.49176	0	0	1_α	1_α	0	0	1_α	1_α
	0.50311	0	1_α	1_α	0	0	1_α	0	1_α
	-0.48704	1_α	0	0	1_α	1_α	0	1_α	0
1^5B_2	0.49445	0	1_α	1_α	0	0	0	1_α	1_α
	-0.50538	1_α	0	0	1_α	1_α	1_α	0	0
	0.49311	1_α	1_α	0	0	1_α	0	1_α	0
	0.50674	0	0	1_α	1_α	0	1_α	0	1_α
2^5B_2	0.39584	0	1_α	1_α	0	1_α	1_α	0	0
	0.59078	1_α	0	0	1_α	0	0	1_α	1_α
	0.57180	1_α	1_α	0	0	0	1_α	0	1_α
	-0.40886	0	0	1_α	1_α	1_α	0	1_α	0
3^5B_2	0.49317	0	1_α	1_α	0	0	0	1_α	1_α
	0.50677	1_α	0	0	1_α	1_α	1_α	0	0
	-0.49441	1_α	1_α	0	0	1_α	0	1_α	0
	0.50531	0	0	1_α	1_α	0	1_α	0	1_α
4^5B_2	0.50668	0	1_α	1_α	0	0	0	1_α	1_α
	0.49309	1_α	0	0	1_α	1_α	1_α	0	0
	0.50540	1_α	1_α	0	0	1_α	0	1_α	0
	-0.49450	0	0	1_α	1_α	0	1_α	0	1_α
1^5B_1	0.50656	1_α	0	1_α	1_α	0	1_α	0	0
	0.48722	1_α	1_α	1_α	0	0	0	1_α	0
	-0.49336	0	1_α	0	0	1_α	0	1_α	1_α
	0.50017	0	0	0	1_α	1_α	1_α	0	1_α

		Orbital occupation							
State	**Weight**	**1a$_1$**	**2a$_1$**	**1b$_2$**	**2b$_2$**	**1b$_1$**	**2b$_1$**	**1a$_2$**	**2a$_2$**
2^5B_1	-0.31250	0	1_α	1_α	1_α	1_α	0	0	0
	0.44855	1_α	1_α	0	1_α	0	0	0	1_α
	0.68759	1_α	0	0	0	0	1_α	1_α	1_α
	0.46657	0	0	1_α	0	1_α	1_α	1_α	0
1^5A_2	-0.49044	1_α	1_α	1_α	0	0	1_α	0	0
	0.50938	1_α	0	1_α	1_α	0	0	1_α	0
	0.50938	0	0	0	1_α	1_α	0	1_α	1_α
	0.49044	0	1_α	0	0	1_α	1_α	0	1_α
2^5A_2	0.38994	1_α	1_α	0	1_α	1_α	0	0	0
	-0.38994	0	1_α	1_α	1_α	0	0	0	1_α
	0.58987	0	0	1_α	0	0	1_α	1_α	1_α
	0.58987	1_α	0	0	0	1_α	1_α	1_α	0
1^3A_1	-0.34663	1_α	1_β	0	0	1_α	1_α	0	0
	0.36026	0	0	1_α	1_β	0	0	1_α	1_α
	0.34667	0	1_α	1_β	0	0	1_α	0	1_α
	-0.36024	1_α	0	0	1_β	1_α	0	1_α	0
2^3A_1	-0.48160	1_α	0	1_α	0	0	1_β	1_α	0
	0.34072	1_α	0	1_α	0	0	1_α	1_β	0
	-0.41710	0	0	0	0	1_α	1_β	1_α	1_α
	0.34057	0	0	0	0	1_α	1_α	1_α	1_β
1^3B_2	0.34985	0	1_α	1_β	0	0	0	1_α	1_α
	0.35716	1_α	0	0	1_β	1_α	1_α	0	0
	-0.34980	1_α	1_β	0	0	1_α	0	1_α	0
	-0.35717	0	0	1_α	1_β	0	1_α	0	1_α
2^3B_2	-0.41919	1_α	0	0	1_β	0	0	1_α	1_α
	-0.40454	1_α	1_β	0	0	0	1_α	0	1_α
	0.34228	1_α	0	0	1_α	0	0	1_α	1_β
	0.33033	1_α	1_α	0	0	0	1_α	0	1_β
1^3B_1	0.41351	1_α	0	1_α	1_β	0	1_α	0	0
	-0.33192	1_α	1_β	1_α	0	0	0	1_α	0
	-0.34887	0	1_α	0	0	1_β	0	1_α	1_α
	0.34063	0	0	0	1_α	1_β	1_α	0	1_α
2^3B_1	0.30537	1_α	1_β	0	1_α	0	0	0	1_α
	0.48617	1_α	0	0	0	0	1_β	1_α	1_α
	-0.32158	1_α	0	0	0	0	1_α	1_α	1_β
	-0.36705	0	0	1_α	0	1_α	1_β	1_α	0
1^3A_2	0.34664	1_α	1_β	1_α	0	0	1_α	0	0
	0.41596	1_α	0	1_α	1_β	0	0	1_α	0
	0.36025	0	0	0	1_α	1_β	0	1_α	1_α
	0.34668	0	1_α	0	0	1_β	1_α	0	1_α
2^3A_2	0.41710	0	0	1_α	0	0	1_β	1_α	1_α
	-0.34057	0	0	1_α	0	0	1_α	1_α	1_β
	-0.48160	1_α	0	0	0	1_α	1_β	1_α	0
	0.34072	1_α	0	0	0	1_α	1_α	1_β	0

S9.2 Diamond-shaped $[NpO_2]_2^{2+}$ - CAS(8,12)SCF.

Table S14: Structure of the calculated states of the diamond-shaped $[NpO_2]_2^{2+}$ cluster.

		Orbital occupation											
State	**Weight**	**1a$_g$**	**2a$_g$**	**3a$_g$**	**4a$_g$**	**1a$_u$**	**2a$_u$**	**1b$_u$**	**2b$_u$**	**3b$_u$**	**4b$_u$**	**1b$_g$**	**2b$_g$**
1^5A_g	0.53801	2	1_α	0	0	1_α	0	2	1_α	0	0	0	1_α
	0.42115	2	0	1_α	0	0	1_α	2	0	1_α	0	1_α	0
2^5A_g	-0.44722	2	1_α	1_α	0	0	0	2	1_α	1_α	0	0	0
	0.51232	2	0	0	0	1_α	1_α	2	0	0	0	1_α	1_α
1^5A_u	-0.33321	2	1_α	0	0	1_α	0	2	1_α	1_α	0	0	0
	-0.35649	2	1_α	0	0	1_α	0	2	0	0	0	1_α	1_α
	-0.32388	2	0	1_α	0	0	1_α	2	1_α	1_α	0	0	0
	-0.34650	2	0	1_α	0	0	1_α	2	0	0	0	1_α	1_α
	-0.32486	2	1_α	1_α	0	0	0	2	0	1_α	0	1_α	0
	-0.33227	2	1_α	1_α	0	0	0	2	1_α	0	0	0	1_α
	0.34749	2	0	0	0	1_α	1_α	2	0	1_α	0	1_α	0
	0.35543	2	0	0	0	1_α	1_α	2	1_α	0	0	0	1_α
2^5A_u	-0.38758	2	0	1_α	0	1_α	0	2	1_α	1_α	0	0	0
	-0.41482	2	0	1_α	0	1_α	0	2	0	0	0	1_α	1_α
	-0.38444	2	1_α	1_α	0	0	0	2	0	1_α	0	0	1_α
	0.41132	2	0	0	0	1_α	1_α	2	0	1_α	0	0	1_α
1^5B_u	-0.39955	2	0	1_α	0	1_α	1_α	2	0	1_α	0	0	0
	0.40591	2	1_α	1_α	0	1_α	0	2	0	0	0	0	1_α
	-0.39616	2	0	1_α	0	0	0	2	0	1_α	0	1_α	1_α
	-0.40251	2	0	0	0	1_α	0	2	1_α	1_α	0	0	1_α
2^5B_u	0.33963	2	1_α	0	0	1_α	1_α	2	0	1_α	0	0	0
	-0.34443	2	0	1_α	0	1_α	1_α	2	1_α	0	0	0	0
	-0.34547	2	1_α	1_α	0	1_α	0	2	0	0	0	1_α	0
	0.33829	2	1_α	1_α	0	0	1_α	2	0	0	0	0	1_α
	-0.33782	2	1_α	0	0	0	0	2	0	1_α	0	1_α	1_α
	0.34010	2	0	1_α	0	0	0	2	1_α	0	0	1_α	1_α
	-0.34087	2	0	0	0	1_α	0	2	1_α	1_α	0	1_α	0
	0.33687	2	0	0	0	0	1_α	2	1_α	1_α	0	0	1_α
1^5B_g	0.33576	2	1_α	1_α	0	1_α	0	2	1_α	0	0	0	0
	0.32438	2	1_α	1_α	0	0	1_α	2	0	1_α	0	0	0
	0.35642	2	1_α	0	0	1_α	1_α	2	0	0	0	0	1_α
	0.35038	2	0	1_α	0	1_α	1_α	2	0	0	0	1_α	0
	0.35464	2	0	0	0	1_α	0	2	1_α	0	0	1_α	1_α
	0.34308	2	0	0	0	0	1_α	2	0	1_α	0	1_α	1_α
	-0.32906	2	1_α	0	0	0	0	2	1_α	1_α	0	0	1_α
	-0.32307	2	0	1_α	0	0	0	2	1_α	1_α	0	1_α	0
2^5B_g	-0.38825	2	1_α	1_α	0	1_α	0	2	0	1_α	0	0	0
	-0.41604	2	0	1_α	0	1_α	1_α	2	0	0	0	0	1_α
	-0.41007	2	0	0	0	1_α	0	2	0	1_α	0	1_α	1_α
	0.38378	2	0	1_α	0	0	0	2	1_α	1_α	0	0	1_α
1^3A_g	0.20535	2	1_α	1_α	0	2	0	2	0	0	0	0	0
	-0.20133	2	0	2	0	1_α	1_α	2	0	0	0	0	0
	-0.20366	2	0	0	0	2	0	2	1_α	1_α	0	0	0
	-0.20063	2	1_α	1_α	0	0	0	2	0	0	0	0	2
	0.24627	2	1_α	0	0	1_α	0	2	0	1_β	0	0	1_α
	0.23127	2	0	1_α	0	1_α	0	2	0	1_α	0	1_β	0
	-0.24861	2	0	1_α	0	1_α	0	2	1_β	0	0	0	1_α
	-0.22786	2	0	1_α	0	0	1_α	2	0	1_α	0	0	1_β

		Orbital occupation											
State	**Weight**	**1a$_g$**	**2a$_g$**	**3a$_g$**	**4a$_g$**	**1a$_u$**	**2a$_u$**	**1b$_u$**	**2b$_u$**	**3b$_u$**	**4b$_u$**	**1b$_g$**	**2b$_g$**
	-0.28038	2	1_α	1_α	0	1_β	1_α	2	0	0	0	0	0
	0.24104	2	1_α	0	0	1_β	0	2	0	1_α	0	1_α	0
	-0.24384	2	0	1_α	0	1_β	0	2	1_α	0	0	1_α	0
2^3A_g	-0.23759	2	1_α	0	0	0	1_β	2	0	1_α	0	0	1_α
	0.23969	2	0	1_α	0	0	1_β	2	1_α	0	0	0	1_α
	0.27795	2	1_α	1_α	0	0	0	2	0	0	0	1_β	1_α
	0.27806	2	0	0	0	1_α	1_α	2	1_β	1_α	0	0	0
	0.27584	2	0	0	0	0	0	2	1_α	1_α	0	1_β	1_α
	-0.19186	2	1_α	0	0	1_α	0	2	1_α	1_β	0	0	0
	0.21832	2	1_α	0	0	1_α	0	2	0	0	0	1_β	1_α
	0.19768	2	0	1_α	0	0	1_α	2	1_β	1_α	0	0	0
1^3A_u	-0.19971	2	0	1_α	0	0	1_α	2	0	0	0	1_α	1_β
	0.19133	2	1_α	1_α	0	0	0	2	1_α	0	0	0	1_β
	0.21325	2	0	0	0	1_α	1_α	2	0	1_β	0	1_α	0
	0.21720	2	0	0	0	1_α	1_α	2	1_β	0	0	0	1_α
	0.20998	2	0	1_α	0	2	1_α	2	0	0	0	0	0
	0.20732	2	0	0	0	2	0	2	0	1_α	0	1_α	0
	-0.23663	2	0	1_α	0	1_α	0	2	1_β	1_α	0	0	0
2^3A_u	-0.25415	2	0	1_α	0	1_α	0	2	0	0	0	1_β	1_α
	0.20559	2	0	1_α	0	0	1_α	2	0	0	0	0	2
	-0.22160	2	1_α	1_α	0	0	0	2	0	1_α	0	0	1_β
	-0.25162	2	0	0	0	1_α	1_α	2	0	1_β	0	0	1_α
	0.27332	2	1_α	0	0	2	0	2	1_α	0	0	0	0
	0.21098	2	0	1_α	0	0	2	2	0	1_α	0	0	0
	-0.27035	2	2	0	0	1_α	0	2	0	0	0	0	1_α
1^3B_u	-0.21319	2	0	2	0	0	1_α	2	0	0	0	1_α	0
	0.26702	2	1_α	0	0	0	0	2	1_α	0	0	0	2
	0.21083	2	0	1_α	0	0	0	2	0	1_α	0	2	0
	-0.26964	2	0	0	0	1_α	0	2	2	0	0	0	1_α
	-0.20871	2	0	0	0	0	1_α	2	0	2	0	1_α	0
	-0.22450	2	2	1_α	0	0	0	2	0	1_α	0	0	0
	0.22663	2	1_α	2	0	0	0	2	1_α	0	0	0	0
	-0.25976	2	0	0	0	2	1_α	2	0	0	0	1_α	0
2^3B_u	0.25669	2	0	0	0	1_α	2	2	0	0	0	0	1_α
	0.22191	2	1_α	0	0	0	0	2	1_α	2	0	0	0
	-0.22395	2	0	1_α	0	0	0	2	2	1_α	0	0	0
	-0.25660	2	0	0	0	1_α	0	2	0	0	0	2	1_α
	0.25384	2	0	0	0	0	1_α	2	0	0	0	1_α	2
	-0.20556	2	1_α	1_α	0	1_β	0	2	1_α	0	0	0	0
1^3B_g	-0.24739	2	0	1_α	0	1_β	1_α	2	0	0	0	1_α	0
	0.21867	2	1_α	0	0	1_α	1_β	2	0	0	0	0	1_α
	0.21702	2	0	0	0	1_α	0	2	1_α	0	0	1_β	1_α
	-0.23756	2	1_α	1_α	0	1_β	0	2	0	1_α	0	0	0
	0.20774	2	0	0	0	2	1_α	2	0	1_α	0	0	0
	-0.20959	2	0	1_α	0	2	0	2	0	0	0	1_α	0
2^3B_g	0.25368	2	0	1_α	0	1_α	1_β	2	0	0	0	0	1_α
	0.25124	2	0	0	0	1_α	0	2	0	1_α	0	1_β	1_α
	-0.20312	2	0	0	0	0	1_α	2	0	1_α	0	0	2
	-0.22165	2	0	1_α	0	0	0	2	1_α	1_α	0	0	1_β
	-0.20567	2	0	1_α	0	0	0	2	0	0	0	1_α	2

S9.3 Diamond-shaped $[NpO_2]_2^{2+}$ - CAS(4,8)SCF.

Table S15: Composition of the wave functions of the diamond-shaped $[NpO_2]_2^{2+}$ complex.

		Orbital occupation							
State	**Weight**	**2a$_g$**	**3a$_g$**	**1a$_u$**	**2a$_u$**	**2b$_u$**	**3b$_u$**	**1b$_g$**	**2b$_g$**
1^5A_g	0.56202	1_α	0	1_α	0	1_α	0	0	1_α
	0.43186	0	1_α	0	1_α	0	1_α	1_α	0
2^5A_g	0.46257	1_α	1_α	0	0	1_α	1_α	0	0
	-0.53162	0	0	1_α	1_α	0	0	1_α	1_α
1^5A_u	0.34545	1_α	0	1_α	0	1_α	1_α	0	0
	0.37010	1_α	0	1_α	0	0	0	1_α	1_α
	0.33588	0	1_α	0	1_α	1_α	1_α	0	0
	0.35984	0	1_α	0	1_α	0	0	1_α	1_α
	0.33681	1_α	1_α	0	0	0	1_α	1_α	0
	0.34450	1_α	1_α	0	0	1_α	0	0	1_α
	-0.36085	0	0	1_α	1_α	0	1_α	1_α	0
	-0.36908	0	0	1_α	1_α	1_α	0	0	1_α
2^5A_u	0.40367	0	1_α	1_α	0	1_α	1_α	0	0
	0.43264	0	1_α	1_α	0	0	0	1_α	1_α
	0.40067	1_α	1_α	0	0	0	1_α	0	1_α
	-0.42937	0	0	1_α	1_α	0	1_α	0	1_α
1^5B_u	-0.41653	0	1_α	1_α	1_α	0	1_α	0	0
	0.42302	1_α	1_α	1_α	0	0	0	0	1_α
	-0.41335	0	1_α	0	0	0	1_α	1_α	1_α
	-0.41994	0	0	1_α	0	1_α	1_α	0	1_α
2^5B_u	0.35267	1_α	0	1_α	1_α	0	1_α	0	0
	-0.35707	0	1_α	1_α	1_α	1_α	0	0	0
	-0.35805	1_α	1_α	1_α	0	0	0	1_α	0
	0.35132	1_α	1_α	0	1_α	0	0	0	1_α
	-0.35087	1_α	0	0	0	0	1_α	1_α	1_α
	0.35320	0	1_α	0	0	1_α	0	1_α	1_α
	-0.35400	0	0	1_α	0	1_α	1_α	1_α	0
	0.35002	0	0	0	1_α	1_α	1_α	0	1_α
1^5B_g	0.34787	1_α	1_α	1_α	0	1_α	0	0	0
	0.33642	1_α	1_α	0	1_α	0	1_α	0	0
	0.37008	1_α	0	1_α	1_α	0	0	0	1_α
	0.36359	0	1_α	1_α	1_α	0	0	1_α	0
	0.36838	0	0	1_α	0	1_α	0	1_α	1_α
	0.35667	0	0	0	1_α	0	1_α	1_α	1_α
	-0.34157	1_α	0	0	0	1_α	1_α	0	1_α
	-0.33519	0	1_α	0	0	1_α	1_α	1_α	0
2^5B_g	0.40429	1_α	1_α	1_α	0	0	1_α	0	0
	0.43379	0	1_α	1_α	1_α	0	0	0	1_α
	0.42809	0	0	1_α	0	0	1_α	1_α	1_α
	-0.40009	0	1_α	0	0	1_α	1_α	0	1_α
1^3A_g	0.21384	1_α	1_α	2	0	0	0	0	0
	-0.20972	0	2	1_α	1_α	0	0	0	0
	-0.20820	0	2	0	0	0	0	1_α	1_α
	-0.21234	0	0	2	0	1_α	1_α	0	0

	Orbital occupation								
State	**Weight**	**2a$_g$**	**3a$_g$**	**1a$_u$**	**2a$_u$**	**2b$_u$**	**3b$_u$**	**1b$_g$**	**2b$_g$**
2^3A_g	0.29071	1_α	1_α	1_β	1_α	0	0	0	0
	-0.20570	1_α	1_α	1_α	1_β	0	0	0	0
	-0.25024	1_α	0	1_β	0	0	1_α	1_α	0
	0.25292	0	1_α	1_β	0	1_α	0	1_α	0
	0.24689	1_α	0	0	1_β	0	1_α	0	1_α
	-0.24894	0	1_α	0	1_β	1_α	0	0	1_α
	0.272260	0	1_α	0	1_α	1_α	0	0	1_α
	0.20415	1_α	1_α	0	0	0	0	1_α	1_β
	-0.28870	0	0	1_α	1_α	1_β	1_α	0	0
	0.20416	0	0	1_α	1_α	1_α	1_β	0	0
	-0.20451	1_α	0	1_α	0	0	1_α	1_β	0
	0.20653	0	1_α	1_α	0	1_α	0	1_β	0
1^3A_u	0.18769	1_α	0	2	1_α	0	0	0	0
	0.18164	0	1_α	1_α	2	0	0	0	0
	0.16870	0	2	0	0	1_α	0	1_α	0
	0.18618	0	0	2	0	1_α	0	1_α	0
2^3A_u	0.20397	1_α	2	1_α	0	0	0	0	0
	0.21880	0	1_α	2	1_α	0	0	0	0
	0.20134	0	2	0	0	1_α	0	0	1_α
	0.21629	0	0	2	0	0	1_α	1_α	0
1^3B_u	-0.28578	1_α	0	2	0	1_α	0	0	0
	-0.20223	1_α	0	1_α	1_β	0	1_α	0	0
	-0.21687	0	1_α	0	2	0	1_α	0	0
	0.28288	2	0	1_α	0	0	0	0	1_α
	0.21891	0	2	0	1_α	0	0	1_α	0
2^3B_u	-0.23263	2	1_α	0	0	0	1_α	0	0
	0.23465	1_α	2	0	0	1_α	0	0	0
	0.20555	1_α	1_α	1_β	0	0	0	1_α	0
	-0.26989	0	0	2	1_α	0	0	1_α	0
	-0.20330	1_α	1_α	0	1_β	0	0	0	1_α
	0.26699	0	0	1_α	2	0	0	0	1_α
	0.23017	1_α	0	0	0	1_α	2	0	0
1^3B_g	0.21298	1_α	1_α	1_β	0	1_α	0	0	0
	0.20594	1_α	1_α	0	1_β	0	1_α	0	0
	0.25676	0	1_α	1_β	1_α	0	0	1_α	0
	-0.22706	1_α	0	1_α	1_β	0	0	0	1_α
2^3B_g	0.20301	0	2	1_α	0	1_α	0	0	0
	0.24738	1_α	1_α	1_β	0	0	1_α	0	0
	-0.21671	0	0	2	1_α	0	1_α	0	0
	0.276700	0	1_α	1_α	0	1_α	0	1_α	0
	0.21849	0	1_α	2	0	0	0	1_α	0
	0.20196	1_α	0	1_β	1_α	0	0	1_α	0
	-0.26468	0	1_α	1_α	1_β	0	0	0	1_α

S10 DMRG mutual information measurements

S10.1 Diamond-shaped $[NpO_2]_2^{3+}$

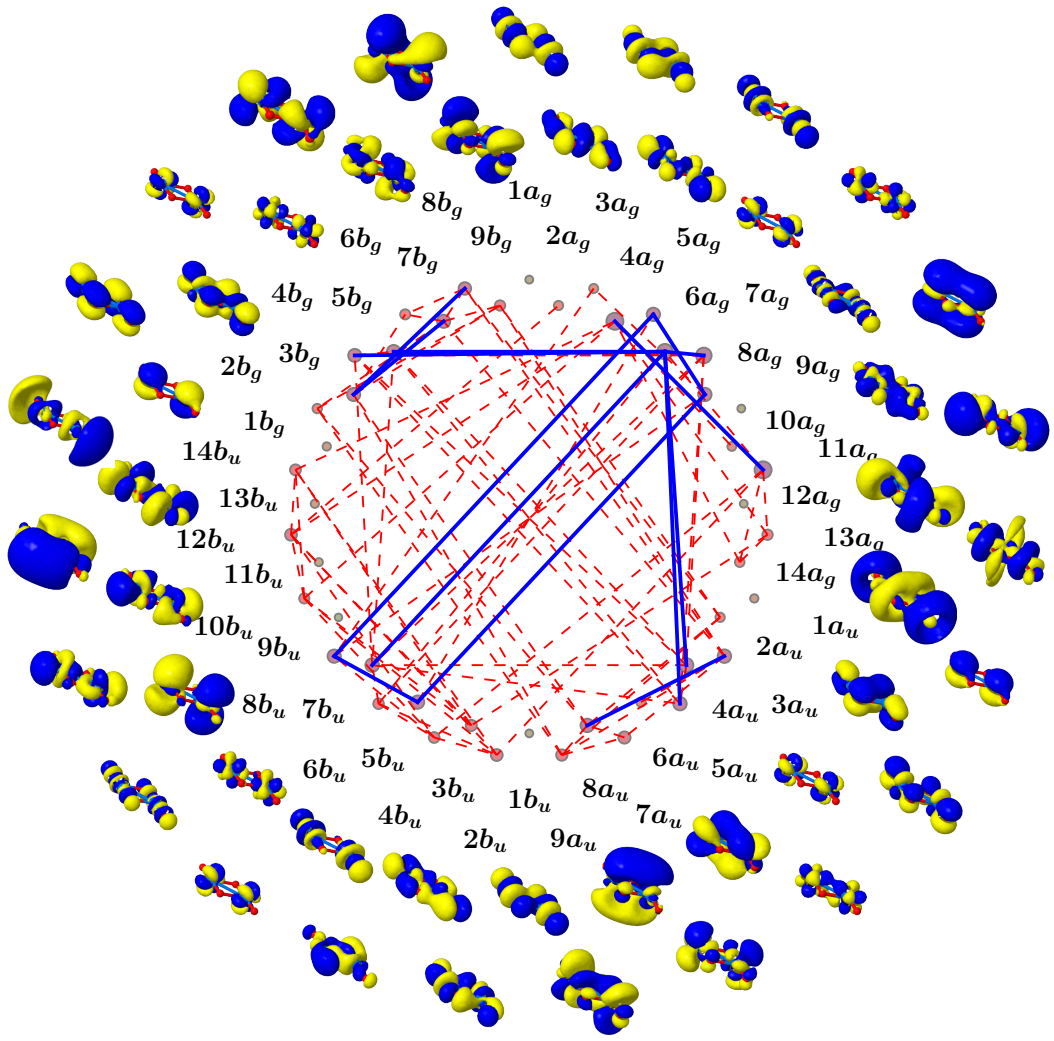


Figure S7: Orbital-pair correlations of the diamond-shaped $[NpO_2]_2^{3+}$. The values of the single-orbital entropy are coded by the size of the dots corresponding to each orbital. The strongest correlated orbitals are connected by blue lines ($I_{i|j} > 10^{-1}$), followed by orbital-pair correlations marked by red lines ($10^{-1} > I_{i|j} > 10^{-2}$).

For diamond-shaped $[NpO_2]_2^{3+}$, 14 occupied orbitals (4 in a_g and in b_u, 3 in a_u and in b_g) and 20 virtual orbitals (6 in a_g and in b_u, 4 in a_u and in b_g) were added to the CASSCF active space (4 in a_g and in b_u, 2 in a_u and in b_g) resulting in a total of 46 molecular orbitals and 35 electrons.

S10.2 Mutual information measurements

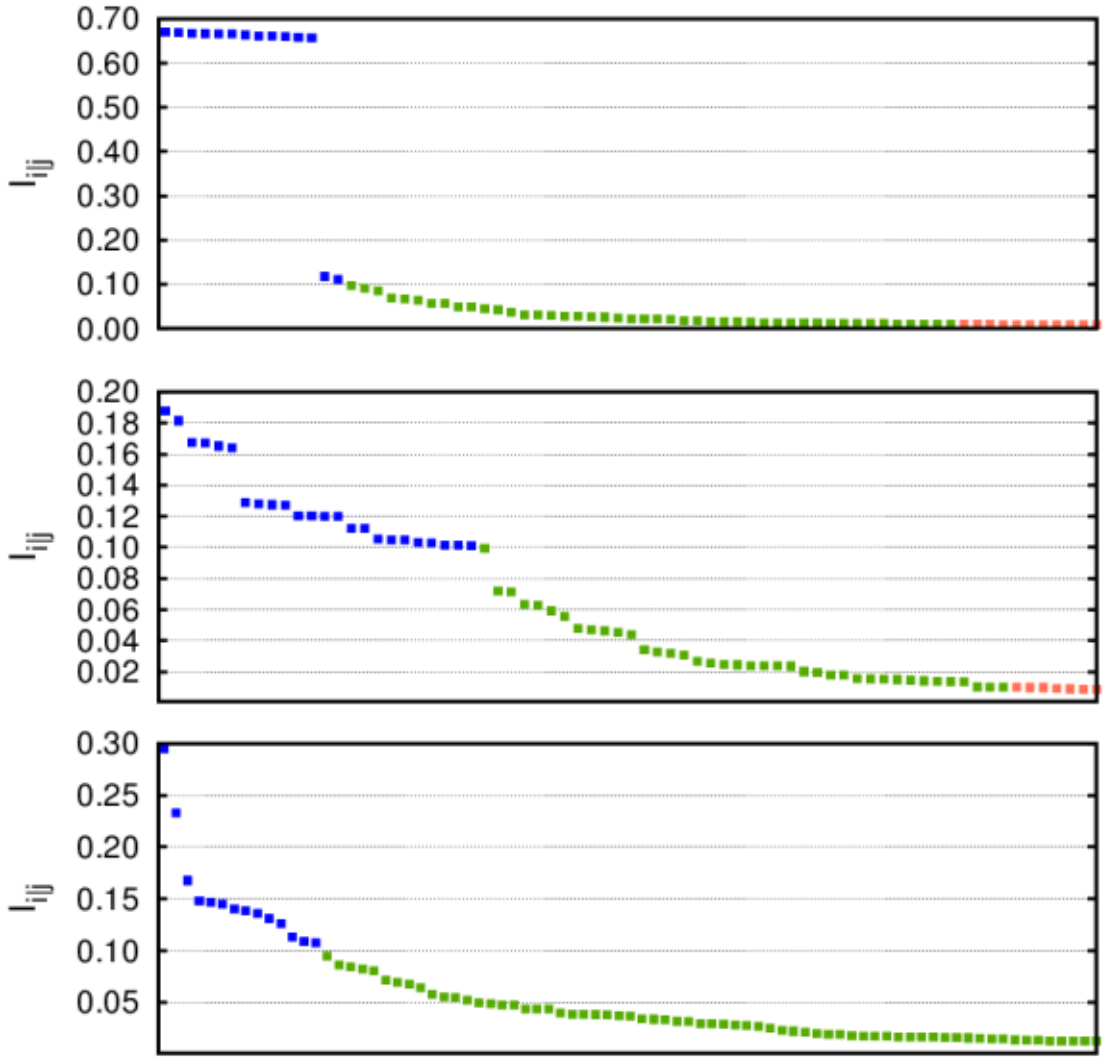


Figure S8: Decaying values of the mutual information (a) for the T-shaped $[NpO_2]_2^{2+}$ (first twelve blue points correspond to the strong correlation between δ_u- and ϕ_u-type orbitals), (b) for the diamond-shaped $[NpO_2]_2^{2+}$ (the first two blue points correspond to the strong correlation between σ_g- and σ_g^*-type orbitals, while the orbital-pair correlation between ϕ_u- and δ_u-type orbitals are marked by next thirteen points), (c) for the diamond-shaped $[NpO_2]_2^{3+}$ (the first blue point corresponds to the strong correlation between orbitals 4 and 11).

S11 Excited states

S11.1 T-shaped cluster in CAS(4,8) calculations

S11.1.1 Spin-free (CASSCF and CASPT2) states in models with explicit water molecules

Table S16: Energetics of the T-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)SCF and CAS(4,8)PT2, using the second-order Douglass-Kroll-Hess Hamiltonian. The geometry of the cluster comes from DFT (BP86) calculations with explicit H_2O molecules and COSMO solvation model. No constraints on symmetry were imposed. For each molecule, the energy differences are calculated with respect to the lowest lying state and are given in cm^{-1}. The first column contains labels assigned to the states.

	Geometry *a*				Geometry *b*	
	$[NpO_2]_2^{2+}$ + $9H_2O$		$[NpO_2]_2^{2+}$ + $5H_2O$			
	CASSCF(4,8)	CAS(4,8)PT2	CAS(4,8)SCF	CAS(4,8)PT2	CASSCF(4,8)	CAS(4,8)PT2
1^5A	0	0	0	0	0	0
2^5A	5	14	0	1	0	1
3^5A	9	14	1	5	1	5
4^5A	14	27	1	23	1	23
5^5A	2400	1599	3335	2614	3335	2608
6^5A	2405	1611	3335	2623	3335	2617
7^5A	2785	2080	3446	2665	3446	2658
8^5A	2794	2091	3447	2666	3447	2660
1^3A	6	6	7	8	7	8
2^3A	11	19	7	8	7	8
3^3A	15	20	8	32	8	32
4^3A	20	33	8	33	8	32
5^3A	2407	1598	3341	2609	3341	2602
6^3A	2412	1609	3341	2609	3341	2603
7^3A	2790	2080	3453	2672	3453	2666
8^3A	2798	2091	3454	2672	3454	2666

S11.1.2 Model with full first coordination shell - geometry *a*

Table S17: Energetics of the T-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)PT2/SO-RASSI, using the second-order Douglass-Kroll-Hess Hamiltonian. The geometry of the cluster comes from DFT (BP86) calculations with 9 explicit H_2O molecules and COSMO solvation model. No constraints on ground-state symmetry were imposed. For each molecule, the energy differences are calculated with respect to the lowest lying state. The first column contains labels assigned to the states.

Label	**ΔE [cm^{-1}]**	**Composition in terms of the spin-free wavefunctions (weight in %)**									
1	0	2^5A	(22)	4^5A	(17)	1^5A	(17)	3^5A	(13)	3^3A	(13)
2	0	4^5A	(22)	3^5A	(17)	2^5A	(17)	1^5A	(13)	1^3A	(13)
3	0	1^5A	(22)	3^5A	(17)	2^5A	(17)	4^5A	(13)	4^3A	(13)
4	0	3^5A	(22)	1^5A	(17)	4^5A	(17)	2^5A	(13)	2^3A	(13)
5	5007	1^5A	(49)	3^3A	(12)	3^5A	(12)	2^5A	(12)	2^3A	(12)
6	5009	3^5A	(49)	1^3A	(12)	1^5A	(12)	4^5A	(12)	4^3A	(12)
7	5014	2^5A	(49)	1^5A	(12)	4^3A	(12)	4^5A	(12)	1^3A	(12)
8	5016	4^5A	(49)	2^3A	(12)	3^5A	(12)	2^5A	(12)	3^3A	(12)
9	6607	5^5A	(49)	6^5A	(49)						
10	6607	5^5A	(49)	6^5A	(49)						
11	6607	5^5A	(24)	5^3A	(24)	6^3A	(24)	6^5A	(24)		
12	6607	6^5A	(24)	5^3A	(24)	5^5A	(24)	6^3A	(24)		
13	7067	7^5A	(49)	8^5A	(49)						

14	7067	7^5A	(49)	8^5A	(49)						
15	7069	7^5A	(25)	8^5A	(25)	7^3A	(24)	8^3A	(24)		
16	7069	7^5A	(25)	8^5A	(25)	7^3A	(24)	8^3A	(24)		
17	8282	3^5A	(24)	1^3A	(15)	4^3A	(15)	2^3A	(11)	2^5A	(10)
18	8283	4^5A	(24)	2^3A	(15)	3^3A	(15)	1^3A	(11)	1^5A	(10)
19	8283	1^5A	(23)	3^3A	(15)	2^3A	(15)	4^3A	(11)	4^5A	(10)
20	8284	2^5A	(23)	4^3A	(15)	1^3A	(15)	3^3A	(11)	3^5A	(10)
21	9052	5^5A	(42)	6^3A	(41)	5^3A	(8)	6^5A	(7)		
22	9052	6^5A	(41)	5^3A	(41)	6^3A	(8)	5^5A	(7)		
23	9528	7^5A	(50)	8^3A	(49)						
24	9528	7^3A	(50)	8^5A	(49)						
25	10801	1^5A	(49)	1^3A	(49)						
26	10815	2^3A	(49)	2^5A	(49)						
27	10815	3^3A	(47)	3^5A	(47)	2^5A	(1)	2^3A	(1)		
28	10824	2^3A	(17)	3^5A	(17)	2^5A	(16)	3^3A	(16)	4^5A	(8)
29	10824	1^3A	(17)	4^5A	(17)	1^5A	(16)	4^3A	(16)	2^3A	(8)
30	10825	4^3A	(28)	4^5A	(26)	1^5A	(19)	1^3A	(18)	3^3A	(1)
31	10826	3^3A	(25)	3^5A	(24)	2^5A	(21)	2^3A	(20)	4^3A	(2)
32	10831	4^3A	(45)	4^5A	(44)	1^5A	(3)	1^3A	(2)	3^3A	(1)
33	12379	5^3A	(48)	5^5A	(48)						
34	12391	6^3A	(48)	6^5A	(48)						
35	12402	5^5A	(49)	5^3A	(49)						
36	12413	6^5A	(49)	6^3A	(49)						
37	12881	7^3A	(49)	7^5A	(49)						
38	12885	7^3A	(49)	7^5A	(49)						
39	12892	8^3A	(49)	8^5A	(49)						
40	12896	8^3A	(49)	8^5A	(49)						
41	13365	1^5A	(22)	3^3A	(15)	2^3A	(13)	4^3A	(12)	2^5A	(12)
42	13368	2^5A	(22)	4^3A	(15)	1^3A	(13)	3^3A	(12)	1^5A	(11)
43	13371	3^5A	(22)	1^3A	(15)	4^3A	(13)	2^3A	(12)	4^5A	(11)
44	13373	4^5A	(22)	2^3A	(15)	3^3A	(13)	1^3A	(12)	3^5A	(11)
45	15719	6^3A	(44)	5^5A	(44)	5^3A	(4)	6^5A	(3)	1^5A	(1)
46	15719	6^5A	(44)	5^3A	(44)	6^3A	(4)	5^5A	(3)	2^5A	(1)
47	16249	8^3A	(49)	7^5A	(49)						
48	16249	8^5A	(49)	7^3A	(49)						
49	16622	3^5A	(49)	4^5A	(12)	1^3A	(12)	1^5A	(12)	4^3A	(12)
50	16629	4^5A	(49)	2^3A	(12)	3^5A	(12)	2^5A	(12)	3^3A	(12)
51	16632	1^5A	(47)	3^3A	(12)	2^5A	(12)	3^5A	(12)	2^3A	(11)
52	16639	2^5A	(47)	4^3A	(12)	1^5A	(12)	4^5A	(12)	1^3A	(11)
53	18176	6^3A	(24)	6^5A	(24)	5^3A	(24)	5^5A	(24)		
54	18176	6^3A	(24)	6^5A	(24)	5^3A	(24)	5^5A	(24)		
55	18180	6^5A	(49)	5^5A	(49)						
56	18180	6^5A	(49)	5^5A	(49)						
57	18710	8^5A	(39)	7^5A	(39)	8^3A	(10)	7^3A	(10)		
58	18710	8^5A	(39)	7^5A	(39)	8^3A	(10)	7^3A	(10)		
59	18711	8^5A	(35)	7^5A	(35)	8^3A	(14)	7^3A	(14)		
60	18711	8^5A	(35)	7^5A	(35)	8^3A	(14)	7^3A	(14)		
61	21645	4^5A	(21)	3^5A	(18)	2^5A	(16)	1^5A	(13)	1^3A	(12)
62	21646	2^5A	(21)	1^5A	(17)	4^5A	(17)	3^5A	(14)	3^3A	(13)
63	21647	3^5A	(21)	4^5A	(18)	1^5A	(16)	2^5A	(13)	2^3A	(12)
64	21647	1^5A	(21)	2^5A	(17)	3^5A	(17)	4^5A	(14)	4^3A	(13)

Table S18: Transitions with non-negligible oscillator strengths.

To	**From**	**Osc. strength** ($\times 10^{-5}$)	**ΔE [cm^{-1}]**	**To**	**From**	**Osc. strength** ($\times 10^{-5}$)	**ΔE [cm^{-1}]**
52	55	1.4576	1541	55	64	1.5924	3467
52	56	1.5325	1541	54	61	2.8242	3469
51	55	1.5257	1548	53	63	2.8225	3471
51	56	1.4609	1548	7	22	1.8222	4038
7	10	2.7560	1593	5	21	1.8188	4045
26	36	10.9910	1598	34	50	1.0388	4238
5	9	2.7375	1600	33	49	1.0416	4243
25	35	10.9174	1601	21	41	1.0314	4313
12	17	1.8342	1675	22	42	1.0256	4316
9	19	2.9252	1676	2	11	1.2227	6607
11	18	1.8275	1676	4	12	1.2221	6607
10	20	2.9130	1677	2	11	1.1734	6607
56	62	1.5937	3466	4	12	1.1734	6607

S11.1.3 Model with five water molecules - geometry *a*

Table S19: Energetics of the T-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)PT2/SO-RASSI, using the second-order Douglass-Kroll-Hess Hamiltonian. The geometry of the cluster comes from DFT (BP86) calculations with 5 explicit H_2O molecules and COSMO solvation model. No constraints on ground-state symmetry were imposed. For each molecule, the energy differences are calculated with respect to the lowest lying state. The first column contains labels assigned to the states.

Label	**ΔE [cm^{-1}]**	**Composition in terms of the spin-free wavefunctions (weight in %)**									
1	0	3^5	(22)	1^5	(17)	4^5	(17)	2^5	(13)	1^3	(13)
2	0	4^5	(22)	3^5	(17)	2^5	(17)	1^5	(13)	2^3	(13)
3	2	1^5	(22)	2^5	(17)	3^5	(17)	4^5	(13)	3^3	(13)
4	3	2^5	(22)	1^5	(17)	4^5	(17)	3^5	(13)	4^3	(13)
5	4952	1^5	(50)	2^5	(12)	3^5	(12)	1^3	(12)	4^3	(12)
6	4955	2^5	(50)	1^5	(12)	4^5	(12)	2^3	(12)	3^3	(12)
7	4957	3^5	(50)	3^3	(12)	4^5	(12)	1^5	(12)	2^3	(11)
8	4964	4^5	(49)	4^3	(12)	3^5	(12)	2^5	(12)	1^3	(11)
9	7529	6^3	(25)	5^3	(25)	5^5	(24)	6^5	(24)		
10	7529	5^3	(25)	6^3	(25)	5^5	(24)	6^5	(24)		
11	7531	5^5	(49)	6^5	(49)						
12	7531	5^5	(49)	6^5	(49)						
13	7641	7^5	(50)	8^5	(49)						
14	7641	7^5	(50)	8^5	(49)						
15	7647	7^5	(25)	8^5	(25)	8^3	(24)	7^3	(24)		
16	7647	7^5	(25)	8^5	(25)	8^3	(24)	7^3	(24)		
17	8183	3^5	(27)	2^3	(18)	3^3	(16)	1^3	(11)	2^5	(11)
18	8184	2^5	(27)	3^3	(18)	2^3	(16)	3^5	(11)	4^3	(11)
19	8184	1^5	(27)	4^3	(18)	1^3	(16)	4^5	(11)	3^3	(11)
20	8186	4^5	(27)	1^3	(18)	4^3	(16)	2^3	(11)	1^5	(11)
21	9965	5^5	(49)	5^3	(27)	6^3	(22)				
22	9969	6^5	(49)	6^3	(27)	5^3	(22)				
23	10058	7^5	(50)	8^3	(49)						
24	10059	8^5	(50)	7^3	(49)						
25	10688	1^5	(49)	2^3	(48)	1^3	(1)				
26	10688	2^5	(49)	1^3	(48)	2^3	(1)				
27	10695	3^5	(25)	1^3	(25)	2^5	(24)	4^3	(23)	2^3	(1)
28	10696	4^3	(26)	2^5	(25)	3^5	(24)	1^3	(22)	2^3	(1)
29	10699	4^5	(25)	2^3	(25)	1^5	(24)	3^3	(23)	1^3	(1)
30	10700	3^3	(26)	1^5	(25)	4^5	(24)	2^3	(22)	1^3	(1)
31	10701	4^3	(49)	3^5	(49)						
32	10710	4^5	(49)	3^3	(49)						
33	13202	2^5	(18)	3^3	(14)	1^5	(13)	4^3	(13)	2^3	(12)
34	13203	1^5	(18)	4^3	(14)	2^5	(13)	3^3	(13)	1^3	(12)
35	13208	3^5	(27)	2^3	(18)	3^3	(16)	1^3	(11)	2^5	(11)
36	13211	4^5	(27)	1^3	(18)	4^3	(16)	2^3	(11)	1^5	(11)
37	13295	5^5	(49)	6^3	(26)	5^3	(23)				
38	13299	6^5	(43)	5^3	(25)	6^3	(23)	5^5	(6)		
39	13302	5^5	(39)	5^3	(26)	6^3	(20)	6^5	(7)	1^5	(1)
40	13306	6^5	(45)	6^3	(25)	5^3	(20)	2^5	(1)	2^3	(1)
41	13351	7^3	(33)	7^5	(32)	8^3	(17)	8^5	(16)		
42	13351	7^3	(33)	7^5	(32)	8^3	(17)	8^5	(16)		
43	13353	8^5	(33)	8^3	(32)	7^5	(17)	7^3	(16)		
44	13353	8^5	(33)	8^3	(32)	7^5	(17)	7^3	(16)		
45	16426	1^5	(49)	2^5	(12)	3^5	(12)	4^3	(12)	1^3	(12)
46	16428	2^5	(49)	1^5	(12)	4^5	(12)	3^3	(12)	2^3	(12)
47	16429	3^5	(49)	3^3	(12)	4^5	(12)	1^5	(12)	2^3	(11)
48	16436	4^5	(49)	4^3	(12)	3^5	(12)	2^5	(12)	1^3	(11)
49	16625	5^5	(49)	5^3	(25)	6^3	(24)				
50	16630	6^5	(49)	6^3	(25)	5^3	(24)				
51	16645	8^3	(50)	7^5	(49)						
52	16646	7^3	(50)	8^5	(49)						
53	19056	8^5	(50)	7^5	(49)						
54	19056	8^5	(50)	7^5	(49)						

Label	ΔE [cm^{-1}]	Composition in terms of the spin-free wavefunctions (weight in %)									
55	19058	7^3	(25)	8^3	(25)	8^5	(24)	7^5	(24)		
56	19058	7^3	(25)	8^3	(25)	8^5	(24)	7^5	(24)		
57	19064	6^5	(25)	5^5	(25)	6^3	(24)	5^3	(24)		
58	19064	6^5	(25)	5^5	(25)	5^3	(24)	6^3	(24)		
59	19071	6^5	(50)	5^5	(49)						
60	19071	6^5	(50)	5^5	(49)						
61	21387	3^5	(22)	4^5	(17)	1^5	(17)	2^5	(13)	1^3	(13)
62	21387	4^5	(22)	3^5	(17)	2^5	(17)	1^5	(13)	2^3	(13)
63	21388	1^5	(22)	2^5	(17)	3^5	(17)	3^3	(13)	4^5	(13)
64	21389	2^5	(22)	4^5	(17)	1^5	(17)	4^3	(13)	3^5	(13)

Table S20: Transitions with non-negligible oscillator strengths.

To	From	Osc. strength ($\times 10^{-5}$)	ΔE [cm^{-1}]	To	From	Osc. strength ($\times 10^{-5}$)	ΔE [cm^{-1}]
61	63	70607	2316	45	48	9.6073	3076
45	47	37106	3075	45	50	3.5694	3272

S11.1.4 Model with five water molecules - geometry *b*.

Table S21: Energetics of the T-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)PT2/SO-RASSI, using the second-order Douglass-Kroll-Hess Hamiltonian. The geometry of the cluster comes from DFT (BP86) calculations with 5 explicit H_2O molecules and COSMO solvation model. No constraints on ground-state symmetry were imposed. For each molecule, the energy differences are calculated with respect to the lowest lying state. The first column contains labels assigned to the states.

Label	ΔE [cm^{-1}]	Composition in terms of the spin-free wavefunctions (weight in %)									
1	0	3^5	(22)	1^5	(17)	4^5	(17)	2^5	(13)	1^3	(13)
2	0	4^5	(22)	3^5	(17)	2^5	(17)	1^5	(13)	2^3	(13)
3	2	1^5	(22)	2^5	(17)	3^5	(17)	4^5	(13)	3^3	(13)
4	3	2^5	(22)	1^5	(17)	4^5	(17)	3^5	(13)	4^3	(13)
5	4952	1^5	(50)	2^5	(12)	3^5	(12)	1^3	(12)	4^3	(12)
6	4955	2^5	(50)	1^5	(12)	4^5	(12)	2^3	(12)	3^3	(12)
7	4957	3^5	(50)	3^3	(12)	4^5	(12)	1^5	(12)	2^3	(11)
8	4964	4^5	(49)	4^3	(12)	3^5	(12)	2^5	(12)	1^3	(11)
9	7529	6^3	(25)	5^3	(25)	5^5	(24)	6^5	(24)		
10	7529	5^3	(25)	6^3	(25)	5^5	(24)	6^5	(24)		
11	7531	5^5	(49)	6^5	(49)						
12	7531	5^5	(49)	6^5	(49)						
13	7641	7^5	(50)	8^5	(49)						
14	7641	7^5	(50)	8^5	(49)						
15	7647	7^5	(25)	8^5	(25)	8^3	(24)	7^3	(24)		
16	7647	7^5	(25)	8^5	(25)	8^3	(24)	7^3	(24)		
17	8183	3^5	(27)	2^3	(18)	3^3	(16)	1^3	(11)	2^5	(11)
18	8184	2^5	(27)	3^3	(18)	2^3	(16)	3^5	(11)	4^3	(11)
19	8184	1^5	(27)	4^3	(18)	1^3	(16)	4^5	(11)	3^3	(11)
20	8186	4^5	(27)	1^3	(18)	4^3	(16)	2^3	(11)	1^5	(11)
21	9965	5^5	(49)	5^3	(27)	6^3	(22)				
22	9969	6^5	(49)	6^3	(27)	5^3	(22)				
23	10058	7^5	(50)	8^3	(49)						
24	10059	8^5	(50)	7^3	(49)						
25	10688	1^5	(49)	2^3	(48)	1^3	(1)				
26	10688	2^5	(49)	1^3	(48)	2^3	(1)				
27	10695	3^5	(25)	1^3	(25)	2^5	(24)	4^3	(23)	2^3	(1)
28	10696	4^3	(26)	2^5	(25)	3^5	(24)	1^3	(22)	2^3	(1)
29	10699	4^5	(25)	2^3	(25)	1^5	(24)	3^3	(23)	1^3	(1)
30	10700	3^3	(26)	1^5	(25)	4^5	(24)	2^3	(22)	1^3	(1)
31	10701	4^3	(49)	3^5	(49)						
32	10710	4^5	(49)	3^3	(49)						
33	13202	2^5	(18)	3^3	(14)	1^5	(13)	4^3	(13)	2^3	(12)
34	13203	1^5	(18)	4^3	(14)	2^5	(13)	3^3	(13)	1^3	(12)

Label	ΔE [cm^{-1}]	Composition in terms of the spin-free wavefunctions (weight in %)									
35	13208	3^5	(27)	2^3	(18)	3^3	(16)	1^3	(11)	2^5	(11)
36	13211	4^5	(27)	1^3	(18)	4^3	(16)	2^3	(11)	1^5	(11)
37	13295	5^5	(49)	6^3	(26)	5^3	(23)				
38	13299	6^5	(43)	5^3	(25)	6^3	(23)	5^5	(6)		
39	13302	5^5	(39)	5^3	(26)	6^3	(20)	6^5	(7)	1^5	(1)
40	13306	6^5	(45)	6^3	(25)	5^3	(20)	2^5	(1)	2^3	(1)
41	13351	7^3	(33)	7^5	(32)	8^3	(17)	8^5	(16)		
42	13351	7^3	(33)	7^5	(32)	8^3	(17)	8^5	(16)		
43	13353	8^5	(33)	8^3	(32)	7^5	(17)	7^3	(16)		
44	13353	8^5	(33)	8^3	(32)	7^5	(17)	7^3	(16)		
45	16426	1^5	(49)	2^5	(12)	3^5	(12)	4^3	(12)	1^3	(12)
46	16428	2^5	(49)	1^5	(12)	4^5	(12)	3^3	(12)	2^3	(12)
47	16429	3^5	(49)	3^3	(12)	4^5	(12)	1^5	(12)	2^3	(11)
48	16436	4^5	(49)	4^3	(12)	3^5	(12)	2^5	(12)	1^3	(11)
49	16625	5^5	(49)	5^3	(25)	6^3	(24)				
50	16630	6^5	(49)	6^3	(25)	5^3	(24)				
51	16645	8^3	(50)	7^5	(49)						
52	16646	7^3	(50)	8^5	(49)						
53	19056	8^5	(50)	7^5	(49)						
54	19056	8^5	(50)	7^5	(49)						
55	19058	7^3	(25)	8^3	(25)	8^5	(24)	7^5	(24)		
56	19058	7^3	(25)	8^3	(25)	8^5	(24)	7^5	(24)		
57	19064	6^5	(25)	5^5	(25)	6^3	(24)	5^3	(24)		
58	19064	6^5	(25)	5^5	(25)	5^3	(24)	6^3	(24)		
59	19071	6^5	(50)	5^5	(49)						
60	19071	6^5	(50)	5^5	(49)						
61	21387	3^5	(22)	4^5	(17)	1^5	(17)	2^5	(13)	1^3	(13)
62	21387	4^5	(22)	3^5	(17)	2^5	(17)	1^5	(13)	2^3	(13)
63	21388	1^5	(22)	2^5	(17)	3^5	(17)	3^3	(13)	4^5	(13)
64	21389	2^5	(22)	4^5	(17)	1^5	(17)	4^3	(13)	3^5	(13)

S11.1.5 Model without explicit first coordination shell.

Table 21: Energetics of the T-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)PT2/SO-RASSI, using the second-order Douglass-Kroll-Hess Hamiltonian. The geometry of the cluster comes from DFT (BP86) calculations, where the solution was modelled by COSMO. The point group symmetry of the molecule is C_{2v}. For each molecule, the energy differences are calculated with respect to the lowest lying state. The first column contains labels assigned to the states.

Label	ΔE [cm^{-1}]	Composition in terms of the spin-free wavefunctions (weight in %)									
1	0	1^5B_1	(22)	1^5A_2	(17)	1^5B_2	(17)	1^3A_1	(13)	1^5A_1	(13)
2	1	1^5A_2	(22)	1^5A_1	(17)	1^5B_1	(17)	1^3B_1	(13)	1^5B_2	(13)
3	18	1^5B_2	(22)	1^5B_1	(17)	1^5A_1	(17)	1^5A_2	(13)	1^3A_2	(13)
4	20	1^5A_1	(22)	1^5A_2	(17)	1^5B_2	(17)	1^5B_1	(13)	1^3B_2	(13)
5	4902	1^5A_2	(50)	1^3A_1	(12)	1^5A_1	(12)	1^5B_1	(12)	1^3B_2	(11)
6	4915	1^5A_1	(49)	1^3A_2	(13)	1^5B_2	(12)	1^5A_2	(12)	1^3B_1	(12)
7	4926	1^5B_1	(49)	1^5B_2	(12)	1^3B_1	(12)	1^5A_2	(12)	1^3A_2	(12)
8	4938	1^5B_2	(50)	1^3B_2	(12)	1^5A_1	(12)	1^5B_1	(12)	1^3A_1	(12)
9	6600	2^5A_2	(50)	2^5A_1	(39)	4^5A_1	(6)	4^5B_2	(2)		
10	6612	2^5A_2	(50)	2^5A_1	(39)	4^5A_1	(7)	4^5B_2	(2)		
11	6987	3^5A_1	(50)	2^5B_2	(42)	3^5B_2	(6)				
12	6987	3^5A_1	(50)	2^5B_2	(42)	3^5B_2	(6)				
13	7004	2^5A_2	(28)	2^5A_1	(22)	2^3A_1	(22)	2^3A_2	(21)	4^5B_2	(4)
14	7098	2^3A_2	(25)	2^5A_2	(24)	2^5A_1	(23)	2^3A_1	(23)	4^5B_2	(3)
15	8110	1^5A_2	(27)	1^3B_2	(18)	1^3A_1	(16)	1^5B_2	(11)	1^3B_1	(11)
16	8111	1^5B_1	(27)	1^3A_2	(18)	1^3B_1	(16)	1^5A_1	(11)	1^3A_1	(11)
17	8117	1^5B_2	(28)	1^3A_1	(18)	1^3B_2	(16)	1^5A_2	(11)	1^3A_2	(11)
18	8122	1^5A_1	(27)	1^3B_1	(18)	1^3A_2	(16)	1^5B_1	(11)	1^3B_2	(11)
19	8995	3^5A_1	(50)	2^5B_2	(23)	1^3B_1	(23)	3^5B_2	(3)		
20	8995	3^5A_1	(50)	2^5B_2	(23)	1^3B_1	(23)	3^5B_2	(3)		

21	9249	2^3A_2 (50)	2^5A_1 (38)	4^5A_1 (6)	4^5B_2 (3)	
22	9269	2^5A_2 (52)	2^3A_1 (38)	4^5B_2 (7)	2^5A_1 (1)	
23	9907	1^3B_1 (50)	3^5A_1 (49)			
24	10414	2^3A_2 (30)	2^5A_2 (24)	4^5A_1 (21)	4^5B_2 (21)	
25	10565	1^5B_2 (50)	1^3B_1 (49)			
26	10576	1^3B_1 (23)	1^5A_2 (23)	1^5B_2 (21)	1^3A_2 (20)	1^3A_1 (5)
27	10580	1^3A_2 (26)	1^5B_2 (26)	1^5A_2 (23)	1^3B_1 (23)	
28	10593	1^5A_2 (49)	1^3A_2 (49)			
29	10599	1^5A_1 (45)	1^3A_1 (44)	1^3B_1 (2)	1^5A_2 (2)	1^5B_2 (2)
30	10637	1^3A_1 (26)	1^5B_1 (25)	1^5A_1 (23)	1^3B_2 (23)	
31	10638	1^3B_2 (26)	1^5A_1 (26)	1^5B_1 (23)	1^3A_1 (22)	
32	10673	1^5B_1 (49)	1^3B_2 (49)			
33	11690	2^5A_2 (34)	2^3A_2 (33)	4^5A_1 (31)		
34	13066	2^5A_1 (29)	2^3A_1 (29)	1^5B_1 (11)	1^3A_2 (7)	1^3B_1 (6)
35	13084	1^5B_2 (26)	1^3A_1 (18)	1^3B_2 (15)	1^5A_2 (10)	1^3A_2 (10)
36	13092	1^5A_1 (27)	1^3B_1 (18)	1^3A_2 (15)	1^3B_2 (11)	1^5B_1 (11)
37	13093	2^5B_2 (99)				
38	13099	2^5A_1 (48)	2^3A_1 (48)			
39	13108	1^5A_2 (27)	1^3B_2 (18)	1^3A_1 (16)	1^3B_1 (11)	1^5B_2 (10)
40	13130	2^5B_2 (50)	1^3B_1 (49)			
41	13130	2^5B_2 (50)	1^3B_1 (49)			
42	13143	2^5A_1 (20)	2^3A_1 (20)	1^5B_1 (16)	1^3A_2 (10)	1^3B_1 (10)
43	13582	4^5A_1 (36)	2^5A_1 (33)	4^5B_2 (28)		
44	13928	4^5B_2 (30)	4^5A_1 (30)	2^3A_1 (18)	2^5A_1 (18)	2^5A_2 (1)
45	14445	4^5A_1 (74)	2^5A_1 (23)	2^3A_2 (1)		
46	14503	3^5B_2 (75)	2^5B_2 (23)	3^5A_1 (1)		
47	14503	3^5B_2 (75)	2^5B_2 (23)	3^5A_1 (1)		
48	14669	3^5B_2 (82)	1^3B_1 (8)	2^5B_2 (7)	3^5A_1 (2)	
49	14670	3^5B_2 (82)	1^3B_1 (8)	2^5B_2 (7)	3^5A_1 (2)	
50	14681	4^5B_2 (75)	4^5A_1 (9)	2^3A_1 (6)	2^5A_1 (6)	2^5A_2 (2)
51	14776	4^5B_2 (78)	2^3A_1 (5)	2^5A_2 (5)	2^5A_1 (5)	4^5A_1 (3)
52	14872	4^5A_1 (44)	2^3A_1 (21)	4^5B_2 (20)	2^5A_2 (6)	2^5A_1 (6)
53	14912	3^5B_2 (99)				
54	15752	2^5B_1 (99)				
55	15753	2^5B_1 (99)				
56	15754	2^5B_1 (99)				
57	15754	2^5B_1 (99)				
58	15754	2^5B_1 (99)				
59	15763	2^3B_2 (99)				
60	15763	2^3B_2 (99)				
61	15763	2^3B_2 (99)				
62	16111	4^5A_1 (53)	4^5B_2 (45)			
63	16117	4^5B_2 (53)	4^5A_1 (46)			
64	16235	1^5B_2 (49)	1^3B_2 (13)	1^5B_1 (12)	1^5A_1 (12)	1^3A_1 (11)
65	16263	1^5A_1 (49)	1^3A_2 (13)	1^5A_2 (12)	1^5B_2 (12)	1^3B_1 (11)
66	16320	1^5B_1 (47)	1^5B_2 (11)	1^3B_1 (11)	1^3A_2 (11)	1^5A_2 (11)
67	16322	1^5A_2 (49)	1^3A_1 (12)	1^3B_2 (12)	1^5A_1 (12)	1^5B_1 (12)
68	16354	4^5A_1 (61)	2^3A_2 (16)	2^5A_2 (9)	4^5B_2 (6)	1^5B_1 (2)
69	16434	3^5A_1 (49)	1^3B_1 (49)			
70	16642	4^5B_2 (38)	2^3A_2 (28)	4^5A_1 (15)	2^5A_2 (13)	2^3A_1 (1)
71	17253	2^3A_2 (47)	2^5A_1 (29)	4^5A_1 (14)	4^5B_2 (8)	
72	17550	3^5A_1 (47)	1^3B_1 (19)	2^5B_2 (18)	3^5B_2 (14)	
73	17551	3^5A_1 (47)	1^3B_1 (19)	2^5B_2 (18)	3^5B_2 (14)	
74	17744	2^5A_2 (40)	4^5B_2 (33)	2^3A_1 (20)	4^5A_1 (4)	2^5A_1 (1)
75	19351	2^5A_2 (25)	2^3A_2 (22)	2^3A_1 (20)	2^5A_1 (20)	4^5B_2 (11)
76	19527	2^5A_2 (29)	2^3A_1 (18)	2^5A_1 (18)	2^3A_2 (17)	4^5B_2 (14)
77	19686	3^5A_1 (47)	2^5B_2 (34)	3^5B_2 (17)		
78	19686	3^5A_1 (47)	2^5B_2 (34)	3^5B_2 (17)		
79	19912	2^5A_2 (48)	2^5A_1 (34)	4^5A_1 (14)	4^5B_2 (3)	
80	19938	2^5A_2 (48)	2^5A_1 (33)	4^5A_1 (13)	4^5B_2 (4)	
81	21186	1^5B_2 (21)	1^5B_1 (17)	1^5A_1 (17)	1^3A_2 (13)	1^5A_2 (13)
82	21195	1^5A_1 (22)	1^5A_2 (17)	1^5B_2 (16)	1^3B_2 (14)	1^5B_1 (13)
83	21204	1^5B_1 (22)	1^5A_2 (17)	1^5B_2 (17)	1^3A_1 (13)	1^5A_1 (13)
84	21210	1^5A_2 (22)	1^5B_1 (17)	1^5A_1 (17)	1^3B_1 (13)	1^5B_2 (13)

Table S22: Transitions with non-negligible oscillator strengths.

To	**From**	**Osc. strength** ($\times 10^{-5}$)	**ΔE** [$\mathbf{cm^{-1}}$]	**To**	**From**	**Osc. strength** ($\times 10^{-5}$)	**ΔE** [$\mathbf{cm^{-1}}$]
43	50	14.5949	1099	19	41	5.5696	4135
70	74	37.6175	1102	20	40	5.5732	4135
22	24	21.4476	1145	41	72	5.0890	4420
21	24	6.0306	1165	40	73	5.0863	4421
43	51	2.0690	1194	33	63	4.6070	4427
52	62	3.2104	1239	24	52	3.0326	4458
51	63	2.6043	1341	52	75	2.2293	4479
68	74	31.1310	1390	52	76	1.1680	4655
66	74	1.2365	1424	45	76	3.5357	5082
52	66	1.1278	1448	51	79	7.1823	5136
52	68	31.0219	1482	51	80	4.4320	5162
53	69	1.9517	1522	46	77	1.2507	5183
62	74	8.9071	1633	47	78	1.2507	5183
74	76	11.5189	1783	50	79	4.6206	5231
33	43	5.8892	1892	50	80	6.9606	5257
71	75	1.0277	2098	44	76	1.3808	5599
45	70	4.7232	2197	43	75	1.3104	5769
33	44	9.5549	2238	33	74	2.5741	6054
13	22	2.4476	2265	14	43	1.2974	6484
71	76	1.0749	2274	24	71	2.1234	6839
22	33	1.6926	2421	22	62	3.2122	6842
44	68	6.1374	2426	13	44	1.7054	6924
43	70	15.5887	3060	22	68	1.1693	7085
24	43	13.6874	3168	22	70	1.8406	7373
33	52	1.9683	3182	21	70	1.2422	7393
23	37	14.4690	3186	10	50	1.4425	8069
63	75	4.5873	3234	9	50	5.7166	8081
37	69	13.7623	3341	10	51	6.1157	8164
24	44	3.3517	3514	9	51	1.4336	8176
68	79	1.7679	3558	14	63	1.6566	9019
62	80	1.4369	3827				

S11.2 Diamond-shaped cluster in calculations with CAS(8,12)

S11.2.1 Model with full first coordination shell - geometry *b*

Table S23: Energetics of the diamond-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)PT2/SO-RASSI. For each molecule, the energy differences are calculated with respect to the lowest lying state. The first column contains labels assigned to the states.

Label	**ΔE [cm^{-1}]**	**Composition in terms of the spin-free wavefunctions (weight in %)**									
1	0	2^5A	(37)	4^5A	(36)	1^5A	(23)	8^5A	(1)		
2	0	2^5A	(37)	4^5A	(36)	1^5A	(23)	8^5A	(1)		
3	4856	3^5A	(44)	1^3A	(22)	2^3A	(10)	4^3A	(10)	3^3A	(4)
4	4857	3^3A	(44)	1^5A	(20)	4^5A	(12)	2^5A	(10)	3^5A	(4)
5	5695	1^3A	(46)	3^5A	(20)	2^3A	(19)	4^3A	(9)	8^3A	(1)
6	5696	1^3A	(45)	3^5A	(20)	2^3A	(19)	4^3A	(9)	1^5A	(1)
7	5698	1^5A	(45)	3^3A	(23)	2^5A	(18)	4^5A	(6)	1^3A	(1)
8	5701	1^5A	(46)	3^3A	(24)	2^5A	(19)	4^5A	(6)	8^5A	(1)
9	5747	4^3A	(39)	2^3A	(28)	3^5A	(27)	1^3A	(1)		
10	5748	4^3A	(39)	2^3A	(28)	3^5A	(28)	1^3A	(1)		
11	5751	4^5A	(42)	2^5A	(29)	3^3A	(24)	1^5A	(1)		
12	5752	4^5A	(43)	2^5A	(29)	3^3A	(24)	1^5A	(1)		
13	7331	8^5A	(42)	7^5A	(40)	1^5A	(7)	6^5A	(6)	2^5A	(1)
14	7331	8^5A	(42)	7^5A	(40)	1^5A	(7)	6^5A	(6)	2^5A	(1)
15	7353	5^5A	(48)	6^5A	(40)	7^5A	(6)	3^5A	(2)	7^3A	(1)
16	7353	5^5A	(48)	6^5A	(40)	7^5A	(6)	3^5A	(2)		
17	7418	5^5A	(25)	8^3A	(24)	6^5A	(23)	7^3A	(23)	7^5A	(2)
18	7420	6^5A	(25)	5^5A	(23)	8^3A	(22)	7^3A	(20)	6^3A	(3)
19	7421	7^5A	(25)	8^5A	(24)	5^3A	(21)	6^3A	(20)	7^3A	(3)
20	7423	8^5A	(25)	5^3A	(23)	6^3A	(23)	7^5A	(23)	6^5A	(2)
21	9718	8^3A	(33)	6^5A	(32)	5^5A	(10)	1^3A	(9)	7^3A	(6)
22	9721	6^3A	(38)	8^5A	(32)	1^5A	(9)	5^3A	(8)	7^5A	(6)
23	9764	7^3A	(37)	5^5A	(37)	6^5A	(6)	8^3A	(6)	7^5A	(5)
24	9772	5^3A	(39)	7^5A	(30)	6^3A	(7)	8^5A	(7)	6^5A	(6)
25	11537	4^5A	(32)	4^3A	(30)	2^3A	(16)	2^5A	(11)	1^5A	(2)
26	11540	4^5A	(29)	4^3A	(28)	2^5A	(18)	2^3A	(15)	7^5A	(2)
27	11545	3^5A	(96)	6^5A	(2)						
28	11545	3^5A	(96)	6^5A	(2)						
29	11551	1^5A	(41)	4^5A	(27)	2^5A	(22)	8^5A	(7)		
30	11551	1^5A	(41)	4^5A	(27)	2^5A	(22)	8^5A	(7)		
31	11559	1^3A	(37)	2^3A	(36)	4^3A	(12)	8^3A	(9)	6^5A	(2)
32	11562	2^5A	(39)	1^5A	(37)	4^5A	(8)	8^5A	(8)	6^3A	(2)
33	13036	5^5A	(48)	8^3A	(43)	1^3A	(6)				
34	13036	5^5A	(48)	8^3A	(43)	1^3A	(6)				
35	13042	5^3A	(48)	8^5A	(42)	1^5A	(6)				
36	13047	5^3A	(48)	8^5A	(43)	1^5A	(6)				
37	13107	6^3A	(46)	7^5A	(34)	6^5A	(13)	2^5A	(1)	7^3A	(1)
38	13110	6^5A	(47)	7^3A	(40)	6^3A	(7)	2^3A	(1)	3^5A	(1)
39	13110	7^3A	(46)	6^5A	(31)	7^5A	(16)	2^3A	(1)	3^5A	(1)
40	13112	7^5A	(43)	6^3A	(41)	7^3A	(6)	6^5A	(3)	2^5A	(1)
41	16300	6^3A	(41)	8^5A	(37)	1^5A	(7)	3^3A	(6)	2^5A	(1)
42	16308	6^5A	(37)	8^3A	(36)	1^3A	(7)	7^5A	(6)	3^5A	(6)
43	16435	5^5A	(39)	7^3A	(36)	5^3A	(9)	7^5A	(9)	6^3A	(1)
44	16436	5^3A	(38)	7^5A	(32)	7^3A	(10)	5^5A	(9)	6^5A	(6)
45	17245	1^3A	(39)	2^3A	(28)	3^5A	(17)	4^3A	(8)	8^3A	(2)
46	17246	1^3A	(38)	2^3A	(28)	3^5A	(14)	4^3A	(11)	8^3A	(2)
47	17250	1^5A	(37)	2^5A	(28)	3^3A	(23)	4^5A	(2)	8^5A	(2)
48	17253	1^5A	(37)	2^5A	(31)	3^3A	(21)	4^5A	(4)	8^5A	(2)
49	17281	4^3A	(39)	3^5A	(30)	2^3A	(19)	1^3A	(4)	7^3A	(1)
50	17284	4^3A	(37)	3^5A	(32)	2^3A	(18)	1^3A	(5)	7^3A	(1)
51	17286	4^5A	(44)	3^3A	(24)	2^5A	(19)	1^5A	(5)	7^5A	(1)
52	17290	4^5A	(44)	3^3A	(26)	2^5A	(16)	1^5A	(7)	7^5A	(1)

Label	ΔE [cm^{-1}]	Composition in terms of the spin-free wavefunctions (weight in %)									
53	18243	3^5A	(39)	1^3A	(15)	4^3A	(11)	2^3A	(9)	8^3A	(7)
54	18248	3^3A	(39)	1^5A	(15)	4^5A	(11)	2^5A	(9)	8^5A	(8)
55	18764	8^5A	(42)	7^5A	(40)	6^5A	(6)	1^5A	(6)	2^5A	(2)
56	18764	8^5A	(42)	7^5A	(40)	6^5A	(6)	1^5A	(6)	2^5A	(2)
57	18876	5^5A	(43)	6^5A	(37)	8^3A	(6)	7^3A	(6)	7^5A	(5)
58	18876	5^5A	(44)	6^5A	(38)	7^5A	(5)	8^3A	(5)	7^3A	(5)
59	18901	8^5A	(26)	6^3A	(23)	5^3A	(22)	7^5A	(21)	6^5A	(3)
60	18904	8^5A	(24)	6^3A	(23)	5^3A	(20)	7^5A	(15)	6^5A	(10)
61	18904	5^5A	(27)	6^5A	(19)	7^3A	(18)	8^3A	(18)	7^5A	(10)
62	18907	5^5A	(28)	6^5A	(25)	8^3A	(20)	7^3A	(19)	7^5A	(4)
63	23075	2^5A	(35)	4^5A	(35)	1^5A	(21)	8^5A	(4)	7^5A	(2)
64	23075	2^5A	(35)	4^5A	(35)	1^5A	(21)	8^5A	(4)	7^5A	(2)

Table S24: Transitions with non-negligible oscillator strengths.

To	From	Osc. strength ($\times 10^{-5}$)	ΔE [cm^{-1}]	To	From	Osc. strength ($\times 10^{-5}$)	ΔE [cm^{-1}]
52	61	1.7546	1614	15	29	2.3256	4198
50	59	1.4272	1617	16	30	2.3265	4198
49	59	1.9271	1620	36	45	2.0773	4198
50	60	1.6123	1620	57	63	1.7124	4199
51	62	2.0061	1621	57	64	2.0929	4199
48	57	2.7718	1623	58	63	2.1964	4199
49	60	1.2519	1623	58	64	1.7976	4199
47	58	2.3714	1626	35	46	1.9917	4204
48	61	8.3025	1651	13	27	2.4772	4214
47	61	1.0065	1654	14	28	2.4826	4214
48	62	1.0781	1654	34	47	2.0653	4214
46	59	7.3448	1655	33	48	1.9674	4217
45	59	4.8194	1656	4	21	1.5757	4861
47	62	9.1374	1657	3	22	1.5761	4865
46	60	4.5678	1658	31	44	1.2880	4877
45	60	7.1054	1659	4	23	2.2032	4907
11	17	2.8112	1667	3	24	2.1870	4916
12	18	2.7004	1668	27	56	1.2661	7219
10	19	2.4192	1673	28	55	1.2593	7219
9	20	2.4747	1676	27	56	1.2489	7219
8	18	10.7752	1719	28	55	1.2425	7219
7	17	11.2455	1720	5	35	1.3057	7347
8	19	1.0177	1720	5	35	1.2626	7347
5	18	1.1216	1725	6	36	1.3102	7351
6	19	4.5070	1725	6	36	1.2656	7351
5	19	5.9852	1726	1	15	1.7912	7353
6	20	6.8120	1727	1	16	1.3440	7353
5	20	4.9743	1728	2	15	1.3403	7353
24	31	6.0348	1787	2	16	1.7965	7353
23	32	5.7914	1798	1	15	1.7512	7353
44	53	5.5577	1807	1	16	1.2469	7353
43	53	5.6502	1808	2	15	1.2437	7353
44	54	5.5967	1812	2	16	1.7560	7353
43	54	5.5375	1813	12	38	1.2122	7358
22	25	2.4894	1816	12	38	1.1390	7358
21	25	3.1685	1819	10	37	1.2840	7359
22	26	3.2333	1819	11	39	1.2651	7359
21	26	2.5552	1822	10	37	1.2254	7359
40	50	1.7566	4172	11	39	1.1864	7359
37	49	2.1274	4174	9	40	1.3118	7365
39	51	1.7253	4176	9	40	1.2433	7365
38	52	1.3302	4180				

S11.2.2 Model without explicit first coordination shell

Table S25: Energetics of the diamond-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(8,12)PT2/SO-RASSI. For each molecule, the energy differences are calculated with respect to the lowest lying state.

The first column contains labels assigned to the states.

Label	**ΔE [cm^{-1}]**	**Composition in terms of the spin-free wavefunctions (weight in %)**				
1	0	2^5A_g (49)	1^5A_g (31)	2^5A_u (17)		
2	0	2^5A_g (49)	1^5A_g (31)	2^5A_u (17)		
3	4821	1^5A_u (49)	2^3A_g (25)	1^3A_g (23)		
4	4830	2^3A_u (49)	2^5A_u (32)	1^5A_g (17)		
5	5687	1^3A_u (43)	1^3A_g (41)	2^3A_g (7)	1^5A_u (6)	
6	5687	1^3A_u (44)	1^3A_g (41)	2^3A_g (8)	1^5A_u (5)	
7	5699	1^5A_u (34)	2^3A_g (33)	1^5A_g (10)	2^5A_g (6)	1^3A_g (6)
8	5700	1^5A_u (41)	2^3A_g (38)	1^3A_g (8)	1^3A_u (5)	1^5A_g (3)
9	5700	1^5A_g (39)	2^5A_g (28)	2^3A_u (11)	1^5A_u (8)	2^3A_g (8)
10	5701	1^5A_g (45)	2^5A_g (34)	2^3A_u (12)	1^5A_u (3)	2^3A_g (3)
11	5709	2^5A_u (49)	2^3A_u (36)	2^5A_g (13)		
12	5711	2^5A_u (49)	2^3A_u (34)	2^5A_g (14)		
13	8097	2^5B_u (49)	2^5B_g (47)	1^5A_g (1)		
14	8097	2^5B_u (49)	2^5B_g (47)	1^5A_g (1)		
15	8104	1^5B_u (49)	1^5B_g (48)			
16	8104	1^5B_u (49)	1^5B_g (48)			
17	8121	1^5B_g (24)	1^5B_u (24)	1^3B_g (23)	2^3B_g (23)	
18	8121	1^3B_u (23)	2^3B_u (23)	2^5B_g (23)	2^5B_u (22)	1^5B_g (2)
19	8122	2^3B_g (23)	1^3B_g (23)	1^5B_u (23)	1^5B_g (22)	2^5B_u (2)
20	8123	2^5B_u (24)	2^5B_g (24)	2^3B_u (24)	1^3B_u (24)	
21	10467	1^5B_g (46)	2^3B_g (43)	1^3A_g (6)	2^3A_g (2)	
22	10482	2^3B_u (45)	2^5B_g (42)	1^5A_g (5)	1^5B_u (3)	1^3B_g (2)
23	10493	1^5B_u (45)	1^3B_g (45)	1^3A_u (3)	2^5B_g (3)	2^3B_u (2)
24	10498	1^3B_u (48)	2^5B_u (47)	2^5A_g (3)		
25	11440	1^3A_u (92)	1^3B_g (2)	1^5A_g (1)	1^5B_u (1)	
26	11441	2^5A_g (96)	2^5B_u (2)	1^3B_u (1)		
27	11444	1^5A_u (98)				
28	11444	1^5A_u (98)				
29	11452	2^3A_g (45)	1^3A_g (44)	2^3B_g (5)	1^5B_g (3)	
30	11459	1^5A_g (56)	2^5A_u (33)	2^5B_g (4)	1^3A_u (2)	2^3B_u (2)
31	11461	2^5A_u (63)	1^5A_g (33)	2^5B_g (2)		
32	11461	2^5A_u (63)	1^5A_g (34)	2^5B_g (2)		
33	13784	1^5B_u (49)	2^3B_g (47)	1^3A_g (2)		
34	13784	1^5B_u (49)	2^3B_g (47)	1^3A_g (2)		
35	13794	1^3B_u (46)	2^5B_g (45)	2^5B_u (2)	2^3B_u (2)	1^5A_g (1)
36	13795	1^3B_u (43)	2^5B_g (42)	2^5B_u (5)	2^3B_u (5)	1^5A_g (1)
37	13804	2^3B_u (44)	2^5B_u (43)	1^3B_u (5)	2^5B_g (5)	
38	13805	2^3B_u (46)	2^5B_u (46)	1^3B_u (2)	2^5B_g (2)	
39	13808	1^5B_g (49)	1^3B_g (49)			
40	13808	1^5B_g (49)	1^3B_g (49)			
41	17008	2^3B_u (39)	2^5B_g (38)	2^5A_u (8)	2^3A_u (6)	2^5A_g (3)
42	17022	1^5B_g (42)	2^3B_g (39)	1^5A_u (8)	1^3A_g (4)	2^3A_g (4)
43	17051	2^5B_u (29)	1^3B_u (29)	2^5A_u (19)	2^3A_u (14)	2^5A_g (5)
44	17058	1^5B_u (29)	1^3B_g (29)	1^5A_u (20)	2^3A_g (13)	1^3A_g (7)
45	17126	1^3A_u (49)	1^3A_g (25)	2^3A_g (23)		
46	17126	1^3A_u (48)	1^3A_g (28)	2^3A_g (19)		
47	17140	1^5A_g (47)	2^5A_g (37)	2^3A_u (11)	2^5B_g (1)	
48	17142	1^5A_g (48)	2^5A_g (31)	2^3A_u (17)	2^5B_g (1)	
49	17147	1^5A_u (45)	2^3A_g (23)	1^3A_g (21)	2^3B_g (4)	1^5B_g (3)
50	17162	2^5A_u (44)	2^3A_u (29)	2^5A_g (14)	2^3B_u (5)	2^5B_g (4)
51	17193	1^5A_u (28)	1^5B_u (21)	1^3B_g (20)	2^3A_g (16)	1^3A_g (11)
52	17208	2^5A_u (29)	2^3A_u (23)	2^5B_u (20)	1^3B_u (19)	2^5A_g (6)
53	18081	1^5A_u (45)	2^3A_g (23)	1^3A_g (20)	2^3B_g (6)	1^5B_g (4)
54	18096	2^3A_u (44)	2^5A_u (29)	1^5A_g (14)	2^5B_g (6)	2^3B_u (4)
55	19490	2^5B_u (48)	2^5B_g (48)	1^5A_g (1)	2^5A_g (1)	
56	19490	2^5B_u (48)	2^5B_g (48)	1^5A_g (1)	2^5A_g (1)	
57	19529	1^5B_g (32)	1^5B_u (32)	2^3B_g (16)	1^3B_g (16)	
58	19530	1^5B_g (33)	1^5B_u (32)	1^3B_g (15)	2^3B_g (15)	1^3B_u (1)
59	19532	2^5B_g (24)	2^5B_u (24)	2^3B_u (23)	1^3B_u (23)	1^5B_u (1)
60	19532	2^5B_g (24)	2^5B_u (24)	2^3B_u (24)	1^3B_u (23)	
61	19538	1^5B_u (41)	1^5B_g (41)	2^3B_g (8)	1^3B_g (8)	
62	19538	1^5B_u (40)	1^5B_g (40)	2^3B_g (9)	1^3B_g (9)	
63	22869	2^5A_g (49)	1^5A_g (30)	2^5A_u (17)	2^5B_g (1)	
64	22869	2^5A_g (49)	1^5A_g (30)	2^5A_u (17)	2^5B_g (1)	

Table S26: Transitions with non-negligible oscillator strengths.

To	**From**	**Osc. strength** ($\times 10^{-5}$)	**ΔE** [**cm**$^{-1}$]	**To**	**From**	**Osc. strength** ($\times 10^{-5}$)	**ΔE** [**cm**$^{-1}$]
41	53	17.2748	1073	45	60	1.8952	2406
42	54	15.5257	1074	46	59	1.5652	2406
43	50	2.2510	111	12	19	3.0679	2411
41	45	9.0094	118	11	17	3.2569	2412
42	48	744.1568	120	7	18	2.7551	2422
41	47	6.0287	132	8	20	3.2557	2423
41	49	93.9031	139	44	59	1.1227	2474
42	50	29.3810	140	50	53	4.1249	919
43	51	363.8878	142	24	25	7.8430	942
44	52	543.1012	150	23	26	6.0518	948
52	57	1.3791	2321	49	54	1.5615	949
51	59	1.4847	2339	23	29	1.5422	959
50	58	1.7933	2368	22	29	17.2553	970
50	62	1.2623	2376	21	30	13.2755	992
49	60	2.1010	2385				

S11.3 Diamond-shaped cluster in calculations with CAS(4,8)

S11.3.1 Model with full first coordination sphere - geometry *b*

Table S27: Energetics of the diamond-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)PT2/SO-RASSI. For each molecule, the energy differences are calculated with respect to the lowest lying state. The first column contains labels assigned to the states.

Label	**ΔE [cm^{-1}]**	**Composition in terms of the spin-free wavefunctions (weight in %)**									
1	0	2^5A	(40)	4^5A	(32)	1^5A	(23)	8^5A	(2)	6^5A	(1)
2	0	2^5A	(40)	4^5A	(32)	1^5A	(23)	8^5A	(2)	6^5A	(1)
3	4900	3^5A	(44)	1^3A	(20)	2^3A	(13)	4^3A	(9)	3^3A	(4)
4	4911	3^3A	(40)	1^5A	(20)	4^5A	(16)	2^5A	(7)	4^3A	(4)
5	5736	1^3A	(33)	3^5A	(17)	1^5A	(15)	2^3A	(11)	2^5A	(7)
6	5736	1^3A	(38)	3^5A	(20)	2^3A	(16)	1^5A	(9)	4^3A	(6)
7	5738	1^5A	(26)	1^3A	(18)	3^3A	(14)	2^5A	(14)	3^5A	(10)
8	5740	1^5A	(42)	2^5A	(22)	3^3A	(18)	4^5A	(5)	1^3A	(3)
9	5798	4^5A	(22)	2^3A	(19)	4^3A	(14)	2^5A	(13)	3^3A	(13)
10	5800	2^3A	(20)	4^5A	(19)	4^3A	(17)	3^5A	(14)	3^3A	(12)
11	5810	4^3A	(28)	4^5A	(21)	3^3A	(14)	2^3A	(12)	2^5A	(11)
12	5811	4^3A	(25)	4^5A	(24)	3^3A	(16)	2^5A	(12)	2^3A	(9)
13	7390	6^5A	(46)	8^5A	(40)	1^5A	(9)	2^5A	(1)		
14	7390	6^5A	(46)	8^5A	(40)	1^5A	(9)	2^5A	(1)		
15	7423	5^5A	(49)	7^5A	(45)	3^5A	(3)				
16	7423	5^5A	(49)	7^5A	(45)	3^5A	(3)				
17	7540	7^5A	(23)	5^5A	(22)	8^3A	(20)	6^3A	(20)	7^3A	(7)
18	7542	6^3A	(18)	5^5A	(13)	6^5A	(13)	7^5A	(11)	8^5A	(11)
19	7543	7^3A	(15)	8^5A	(14)	8^3A	(13)	5^3A	(13)	7^5A	(13)
20	7545	8^5A	(24)	6^5A	(22)	5^3A	(21)	7^3A	(16)	6^3A	(4)
21	9790	7^5A	(41)	6^3A	(18)	1^3A	(13)	7^3A	(9)	8^3A	(8)
22	9817	8^5A	(23)	7^3A	(19)	5^3A	(17)	6^5A	(12)	1^5A	(10)
23	9866	5^3A	(27)	6^5A	(26)	7^3A	(11)	8^5A	(11)	6^3A	(6)
24	9882	5^5A	(40)	8^3A	(29)	6^3A	(8)	6^5A	(3)	2^3A	(3)
25	11654	2^5A	(48)	4^5A	(41)	6^5A	(5)	5^3A	(1)	1^5A	(1)
26	11655	3^5A	(94)	7^5A	(4)						
27	11655	3^5A	(94)	7^5A	(4)						
28	11675	1^5A	(39)	4^5A	(33)	2^5A	(16)	8^5A	(9)	6^5A	(1)
29	11675	1^5A	(39)	4^5A	(33)	2^5A	(16)	8^5A	(9)	6^5A	(1)
30	11682	4^3A	(43)	2^3A	(37)	3^3A	(5)	8^3A	(3)	2^5A	(2)
31	11690	1^5A	(22)	2^3A	(16)	2^5A	(15)	4^5A	(12)	1^3A	(11)
32	11705	1^3A	(23)	4^3A	(19)	1^5A	(12)	2^3A	(10)	2^5A	(8)
33	13134	5^5A	(46)	6^3A	(18)	8^3A	(17)	1^3A	(9)	7^3A	(4)
34	13134	5^5A	(47)	6^3A	(18)	8^3A	(17)	1^3A	(9)	7^3A	(4)
35	13142	5^3A	(46)	8^5A	(39)	1^5A	(8)	5^5A	(1)		
36	13146	5^3A	(47)	8^5A	(40)	1^5A	(9)				
37	13266	6^5A	(38)	7^3A	(34)	7^5A	(8)	6^3A	(6)	8^3A	(5)
38	13269	7^5A	(23)	6^5A	(23)	7^3A	(21)	8^3A	(13)	6^3A	(11)
39	13273	7^5A	(38)	8^3A	(20)	6^3A	(19)	6^5A	(9)	7^3A	(7)
40	13274	7^5A	(23)	6^5A	(23)	7^3A	(20)	6^3A	(13)	8^3A	(13)
41	16415	7^5A	(37)	8^3A	(20)	6^3A	(15)	1^3A	(9)	3^5A	(7)
42	16440	7^3A	(40)	8^5A	(30)	1^5A	(9)	3^3A	(7)	7^5A	(4)
43	16598	5^3A	(48)	6^5A	(47)	8^5A	(1)				
44	16633	5^5A	(48)	6^3A	(27)	8^3A	(21)				
45	17407	1^5A	(21)	2^5A	(21)	2^3A	(16)	1^3A	(13)	3^5A	(6)
46	17409	2^5A	(20)	1^5A	(20)	2^3A	(16)	1^3A	(14)	3^5A	(6)
47	17409	1^3A	(25)	3^5A	(16)	1^5A	(14)	2^5A	(12)	3^3A	(11)
48	17411	1^3A	(24)	3^5A	(15)	1^5A	(14)	2^5A	(13)	3^3A	(10)
49	17446	4^3A	(19)	4^5A	(17)	2^3A	(17)	3^5A	(16)	3^3A	(14)
50	17449	4^3A	(21)	3^5A	(18)	2^3A	(17)	4^5A	(14)	3^3A	(13)

Label	ΔE [cm^{-1}]	Composition in terms of the spin-free wavefunctions (weight in %)									
51	17460	4^5A	(27)	4^3A	(23)	3^3A	(16)	2^5A	(9)	3^5A	(7)
52	17464	4^5A	(29)	4^3A	(20)	3^3A	(18)	2^5A	(9)	3^5A	(7)
53	18447	3^5A	(35)	1^3A	(12)	2^3A	(12)	4^3A	(7)	3^3A	(6)
54	18474	3^3A	(31)	4^5A	(14)	1^5A	(12)	8^5A	(10)	3^5A	(6)
55	18896	6^5A	(45)	8^5A	(40)	1^5A	(8)	2^5A	(4)	4^5A	(1)
56	18896	6^5A	(45)	8^5A	(40)	1^5A	(8)	2^5A	(4)	4^5A	(1)
57	19061	5^5A	(47)	7^5A	(47)	8^3A	(1)	6^3A	(1)		
58	19061	5^5A	(48)	7^5A	(47)	8^3A	(1)	6^3A	(1)	3^5A	(1)
59	19114	8^5A	(25)	6^5A	(24)	7^3A	(23)	5^3A	(22)	6^3A	(2)
60	19116	6^3A	(16)	6^5A	(15)	8^5A	(14)	5^3A	(11)	5^5A	(11)
61	19117	7^5A	(16)	8^3A	(15)	7^3A	(14)	5^5A	(13)	8^5A	(12)
62	19119	7^5A	(25)	8^3A	(24)	5^5A	(23)	6^3A	(21)	7^3A	(1)
63	23307	2^5A	(37)	4^5A	(31)	1^5A	(19)	8^5A	(6)	6^5A	(4)
64	23307	2^5A	(37)	4^5A	(31)	1^5A	(19)	8^5A	(6)	6^5A	(4)

Table S28: Transitions with non-negligible oscillator strengths.

To	From	Osc. strength ($\times 10^{-5}$)	ΔE [cm^{-1}]	To	From	Osc. strength ($\times 10^{-5}$)	ΔE [cm^{-1}]
52	60	2.0944	1652	22	32	1.3244	1888
51	59	1.2788	1654	37	49	1.7062	4180
51	61	1.0667	1657	38	50	1.6832	4180
50	61	2.7621	1668	39	51	1.7662	4187
49	60	1.1991	1670	40	52	1.8944	4190
49	62	2.1688	1673	57	63	1.0766	4246
48	59	5.1408	1703	58	64	1.0831	4246
47	59	3.0043	1705	57	63	2.3750	4246
48	61	5.8523	1706	57	64	1.9293	4246
45	59	2.7339	1707	58	63	1.9410	4246
46	60	7.8175	1707	58	64	2.3897	4246
47	60	2.9530	1707	15	28	2.3120	4252
47	61	2.0025	1708	16	29	2.3119	4252
45	61	2.3462	1710	36	47	1.4696	4263
46	62	1.6772	1710	13	26	1.3116	4265
47	62	3.2402	1710	13	27	1.0262	4265
45	62	5.5806	1712	14	26	1.0232	4265
11	17	1.8176	1730	14	27	1.3134	4265
12	18	1.9549	1731	35	48	1.6119	4269
11	19	1.0185	1733	34	45	1.3577	4273
10	19	1.2276	1743	33	46	1.3736	4275
9	18	1.1479	1744	30	42	1.6606	4758
10	20	2.0361	1745	25	41	1.5008	4761
7	17	3.3861	1802	32	43	1.3171	4893
8	18	3.5966	1802	3	22	1.0488	4917
8	19	4.4553	1803	3	22	2.0094	4917
5	17	5.1432	1804	31	44	1.0274	4943
6	17	2.3997	1804	4	23	1.1914	4955
7	18	1.5200	1804	3	23	1.2323	4966
7	19	4.8301	1805	4	24	1.1709	4971
8	20	2.8362	1805	4	24	2.1942	4971
5	18	4.2717	1806	3	24	1.1064	4982
6	18	1.6206	1806	26	55	1.0778	7241
5	19	1.1810	1807	27	56	1.0809	7241
7	20	1.2520	1807	1	15	1.8893	7423
24	31	1.5055	1808	1	16	1.4599	7423
6	20	6.4798	1809	2	15	1.4591	7423
44	53	2.2384	1814	2	16	1.8906	7423
24	32	3.2965	1823	1	15	1.6474	7423
23	31	3.9313	1824	1	16	1.1988	7423
44	54	7.6799	1841	2	15	1.1981	7423
43	53	7.7835	1849	2	16	1.6484	7423
21	25	5.0584	1864	12	37	1.0856	7455
22	30	3.9665	1865	11	38	1.2190	7459
43	54	2.1414	1876	9	40	1.1393	7476

S11.3.2 Model without explicit solvent

Table S29: Energetics of the diamond-shaped $[NpO_2]_2^{2+}$ molecule calculated with CAS(4,8)PT2/SO-RASSI. For each molecule, the energy differences are calculated with respect to the lowest lying state. The first column contains labels assigned to the states.

Label	**ΔE [cm^{-1}]**	**Composition in terms of the spin-free wavefunctions (weight in %)**				
1	0	2^5A_g (49)	1^5A_g (31)	2^5A_u (17)		
2	0	2^5A_g (49)	1^5A_g (31)	2^5A_u (17)		
3	4856	1^5A_u (49)	2^3A_g (25)	1^3A_g (24)		
4	4870	2^3A_u (49)	2^5A_u (31)	1^5A_g (17)		
5	5732	1^3A_g (48)	1^3A_u (32)	1^5A_u (17)		
6	5732	1^3A_g (48)	1^3A_u (33)	1^5A_u (15)	2^3A_g (1)	
7	5739	1^5A_g (45)	2^5A_g (41)	2^3A_u (7)	2^5A_u (2)	
8	5740	1^5A_g (44)	2^5A_g (43)	2^3A_u (5)	2^5A_u (4)	
9	5742	2^3A_g (48)	1^5A_u (31)	1^3A_u (17)		
10	5743	2^3A_g (48)	1^5A_u (32)	1^3A_u (15)	1^3A_g (1)	
11	5753	2^5A_u (45)	2^3A_u (44)	2^5A_g (5)	1^5A_g (4)	
12	5755	2^5A_u (46)	2^3A_u (42)	2^5A_g (7)	1^5A_g (2)	
13	8135	1^5B_u (49)	2^5B_g (47)	1^5A_g (2)		
14	8135	1^5B_u (49)	2^5B_g (47)	1^5A_g (2)		
15	8147	1^5B_g (49)	2^5B_u (49)	1^5A_u (1)		
16	8147	1^5B_g (49)	2^5B_u (49)	1^5A_u (1)		
17	8181	1^3B_g (23)	2^5B_u (22)	1^5B_g (22)	2^3B_g (20)	1^3B_u (4)
18	8181	1^3B_u (23)	1^5B_u (21)	2^5B_g (21)	1^3B_g (14)	2^3B_u (10)
19	8183	2^3B_g (23)	2^5B_u (21)	1^5B_g (21)	2^3B_u (14)	1^3B_g (10)
20	8183	2^3B_u (23)	1^5B_u (22)	2^5B_g (22)	1^3B_u (20)	2^3B_g (4)
21	10523	2^5B_u (46)	2^3B_g (42)	1^3A_g (7)	2^3A_g (3)	
22	10551	2^3B_u (44)	2^5B_g (39)	1^5A_g (6)	1^5B_g (5)	1^3B_g (1)
23	10560	1^3B_u (47)	1^5B_u (47)	2^5A_g (4)		
24	10563	1^3B_g (45)	1^5B_g (43)	2^5B_g (4)	1^3A_u (4)	2^3B_u (1)
25	11523	1^5A_u (98)	2^5B_u (1)			
26	11523	1^5A_u (98)	2^5B_u (1)			
27	11524	2^5A_g (94)	1^5B_u (3)	1^3B_u (1)		
28	11537	1^3A_u (64)	1^5A_g (18)	2^5A_u (11)	1^3B_g (3)	2^5B_g (1)
29	11544	2^5A_u (62)	1^5A_g (33)	2^5B_g (2)		
30	11544	2^5A_u (63)	1^5A_g (33)	2^5B_g (2)		
31	11546	1^5A_g (38)	1^3A_u (29)	2^5A_u (23)	2^5B_g (3)	2^3B_u (3)
32	11548	2^3A_g (45)	1^3A_g (43)	2^3B_g (6)	2^5B_u (3)	
33	13877	1^5B_g (48)	2^3B_g (46)	1^3A_g (2)	1^3B_u (1)	
34	13878	1^5B_g (48)	2^3B_g (46)	1^3A_g (2)	1^3B_u (1)	
35	13885	1^3B_u (40)	2^5B_g (40)	1^5B_u (7)	2^3B_u (4)	1^3B_g (3)
36	13887	1^3B_u (31)	2^5B_g (31)	1^5B_u (16)	2^3B_u (9)	1^3B_g (6)
37	13893	2^3B_u (33)	1^5B_u (31)	1^3B_u (14)	2^5B_g (14)	2^5B_u (3)
38	13894	2^3B_u (41)	1^5B_u (38)	1^3B_u (6)	2^5B_g (6)	2^5B_u (4)
39	13895	2^5B_u (45)	1^3B_g (41)	2^3B_u (5)	2^5B_g (2)	1^3B_u (2)
40	13895	2^5B_u (44)	1^3B_g (43)	2^3B_u (3)	1^5B_u (2)	2^5B_g (1)
41	17112	2^5B_g (37)	2^3B_u (28)	1^3B_g (11)	2^5A_u (8)	2^3A_u (7)
42	17118	2^5B_u (42)	2^3B_g (39)	1^5A_u (7)	1^3A_g (5)	2^3A_g (4)
43	17165	1^5B_u (31)	1^3B_u (31)	2^5A_u (18)	2^3A_u (12)	2^5A_g (6)
44	17178	1^5B_g (28)	1^5A_u (20)	1^3B_g (20)	2^3A_g (13)	2^3B_u (8)
45	17254	1^3A_u (46)	2^3A_g (23)	1^3A_g (21)	1^5A_g (3)	2^5A_g (2)
46	17255	1^3A_u (47)	1^3A_g (27)	2^3A_g (19)	1^5A_g (1)	2^5A_g (1)
47	17260	1^5A_g (43)	2^5A_g (34)	2^3A_u (11)	1^3A_u (2)	2^3A_g (1)
48	17262	1^5A_g (44)	2^5A_g (36)	2^3A_u (10)	2^5B_g (1)	1^3A_u (1)
49	17267	1^5A_u (47)	1^3A_g (23)	2^3A_g (22)	2^3B_g (3)	2^5B_u (2)
50	17284	2^5A_u (43)	2^3A_u (36)	2^5A_g (8)	2^5B_g (3)	2^3B_u (2)
51	17317	1^5A_u (28)	1^5B_g (21)	2^3A_g (16)	1^3B_g (15)	1^3A_g (11)
52	17330	2^5A_u (30)	2^3A_u (25)	1^5B_u (18)	1^3B_u (18)	2^5A_g (5)
53	18221	1^5A_u (44)	2^3A_g (23)	1^3A_g (19)	2^3B_g (7)	2^5B_u (5)
54	18243	2^3A_u (43)	2^5A_u (28)	1^5A_g (14)	2^5B_g (7)	2^3B_u (4)
55	19600	1^5B_u (48)	2^5B_g (47)	1^5A_g (2)	2^5A_g (1)	
56	19600	1^5B_u (48)	2^5B_g (47)	1^5A_g (2)	2^5A_g (1)	
57	19655	1^5B_g (46)	2^5B_u (46)	2^3B_g (3)	1^3B_g (2)	
58	19655	1^5B_g (46)	2^5B_u (46)	2^3B_g (3)	1^3B_g (2)	

Label	ΔE [cm^{-1}]	Composition in terms of the spin-free wavefunctions (weight in %)				
59	19666	2^5B_g (24)	1^3B_u (24)	1^5B_u (24)	2^3B_u (14)	1^3B_g (10)
60	19666	1^3B_u (24)	2^5B_g (23)	1^5B_u (23)	2^3B_u (13)	1^3B_g (11)
61	19669	2^5B_u (26)	1^5B_g (26)	2^3B_g (21)	2^3B_u (11)	1^3B_g (10)
62	19670	2^5B_u (27)	1^5B_g (27)	2^3B_g (22)	1^3B_g (12)	2^3B_u (9)
63	23029	2^5A_g (48)	1^5A_g (30)	2^5A_u (17)	2^5B_g (1)	1^5B_u (1)
64	23029	2^5A_g (48)	1^5A_g (30)	2^5A_u (17)	2^5B_g (1)	1^5B_u (1)

Table S30: Transitions with non-negligible oscillator strengths.

To	From	Osc. strength ($\times10^{-5}$)	ΔE [cm^{-1}]	To	From	Osc. strength ($\times10^{-5}$)	ΔE [cm^{-1}]
21	28	3.2602	1014	46	59	1.6630	2411
21	31	11.7623	1023	45	60	1.9292	2412
41	53	20.3831	1109	11	17	2.6693	2428
42	54	16.5872	1125	12	19	3.0913	2428
43	50	2.4682	119	9	18	4.5099	2439
42	46	20.8049	137	10	20	4.0084	2440
41	45	1.6595	142	44	59	1.3172	2488
42	48	419.5712	144	43	61	1.1649	2504
41	47	2.9098	148	50	53	3.4635	937
43	51	193.6615	152	48	53	1.4088	959
44	52	722.8882	152	24	27	7.4651	961
41	49	77.0994	155	49	54	1.1689	976
42	50	36.8494	166	23	28	7.2878	977
52	61	1.9496	2339	24	32	1.5833	985
51	59	1.7409	2349	23	31	2.8701	986
50	62	2.7448	2386	22	32	18.8958	997

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