Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Tailoring an efficient computational methodology for studying ligand interactions with heavy radiometals in solution: the case of radium

*Hamissou Mohaman,[a,b] Steffen Happel,[c] Gilles Montavon [b] and Nicolas Galland *[a]*

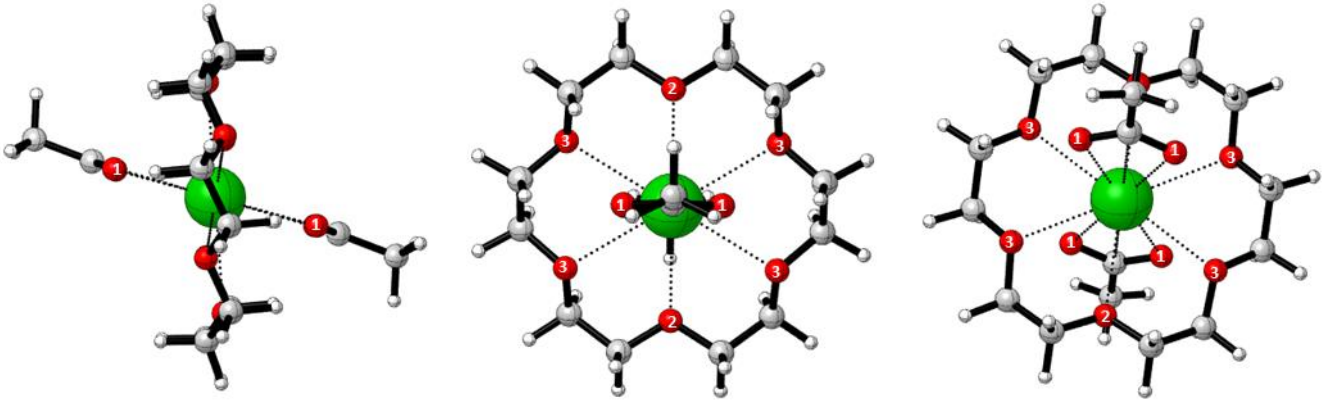
[a] Nantes Université, CNRS, CEISAM UMR 6230, F-44000 Nantes, France.

[b] IMT Atlantique, CNRS, SUBATECH UMR 6457, F-44307 Nantes, France.

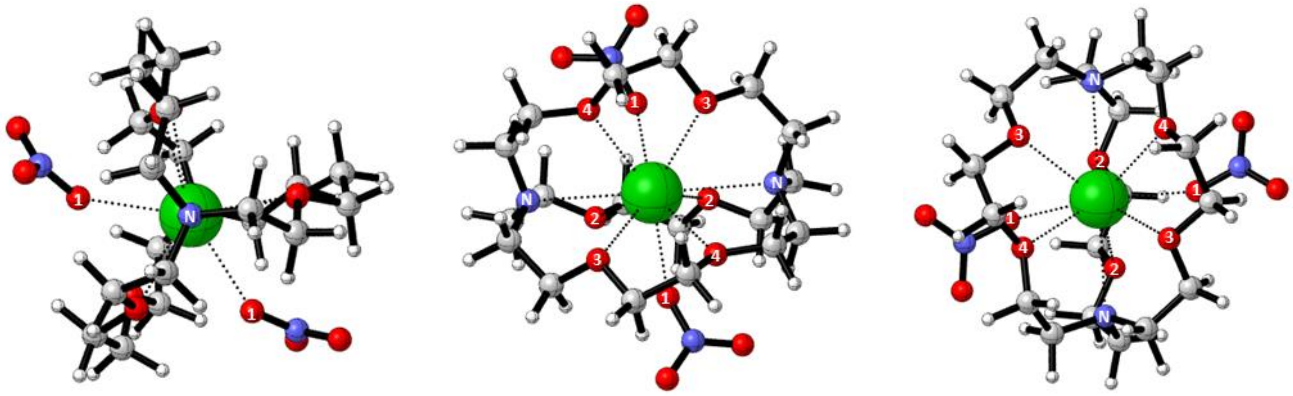
[c] TRISKEM INTERNATIONAL, F-35170 Bruz, France.

Supporting Information

I. Figures



$Ba–O_1$	2.881 Å
$Ba–O_2$	2.753 Å
$Ba–O_3$	2.832 Å



$Ba–O_1$	2.746 Å
$Ba–O_2$	2.807 Å
$Ba–O_3$	2.835 Å
$Ba–O_4$	2.828 Å
Ba–N	3.020 Å

Fig. S1 Different views of the crystallographic reference structures of Ba(II) complexed, corresponding to the CSD entries BIWBAK (top) and AZELOG (bottom). The given interaction distances have been averaged according to the symmetry point groups yield by DFT calculations: C_{2h} symmetry for BIWBAK and C_2 symmetry for AZELOG.

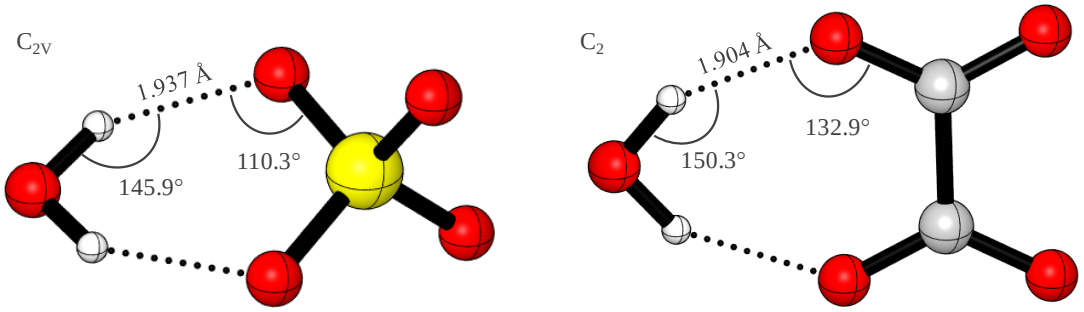


Fig. S2 Computed structure at the SMD sr-MN15/ACVDZ level of theory for the most stable conformer of $[SO_4(H_2O)_1]^{2-}$ (left) and $[C_2O_4(H_2O)_1]^{2-}$ (right).

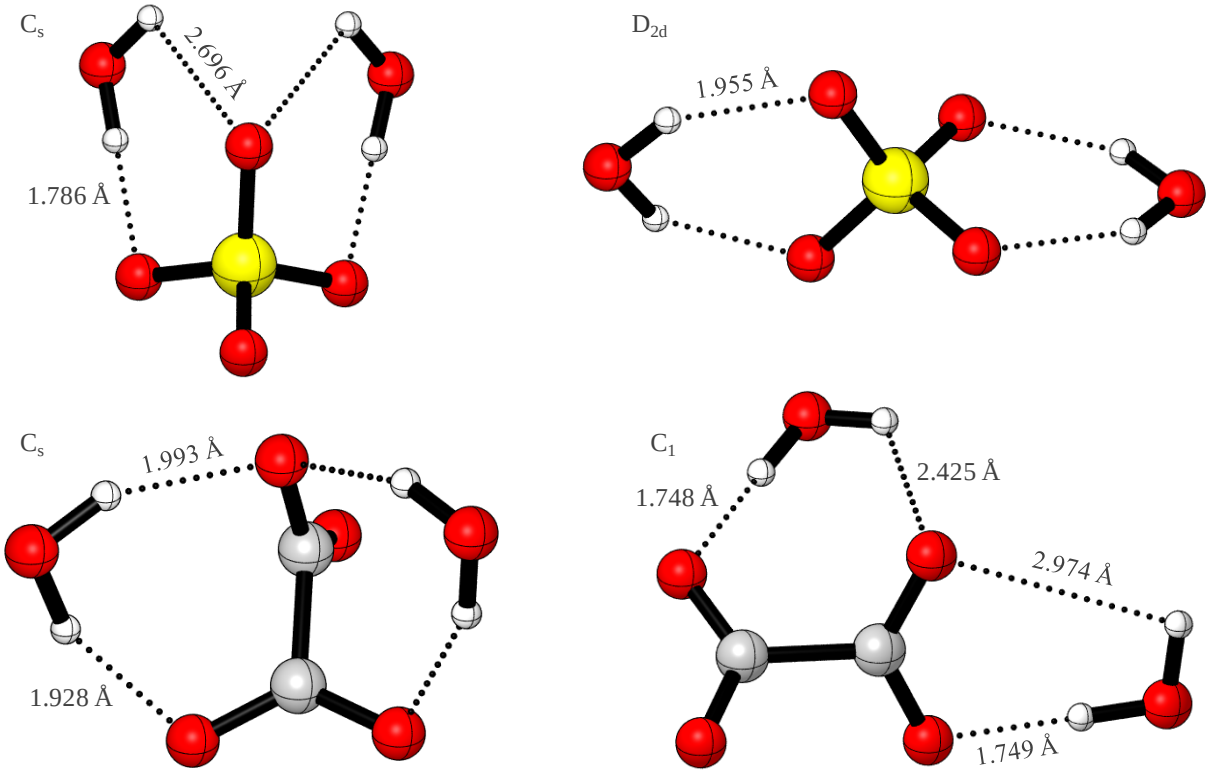


Fig. S3 Computed structure at the SMD sr-MN15/ACVDZ level of theory for the two most stable conformers of $[SO_4(H_2O)_2]^{2-}$ (top) and $[C_2O_4(H_2O)_2]^{2-}$ (bottom).

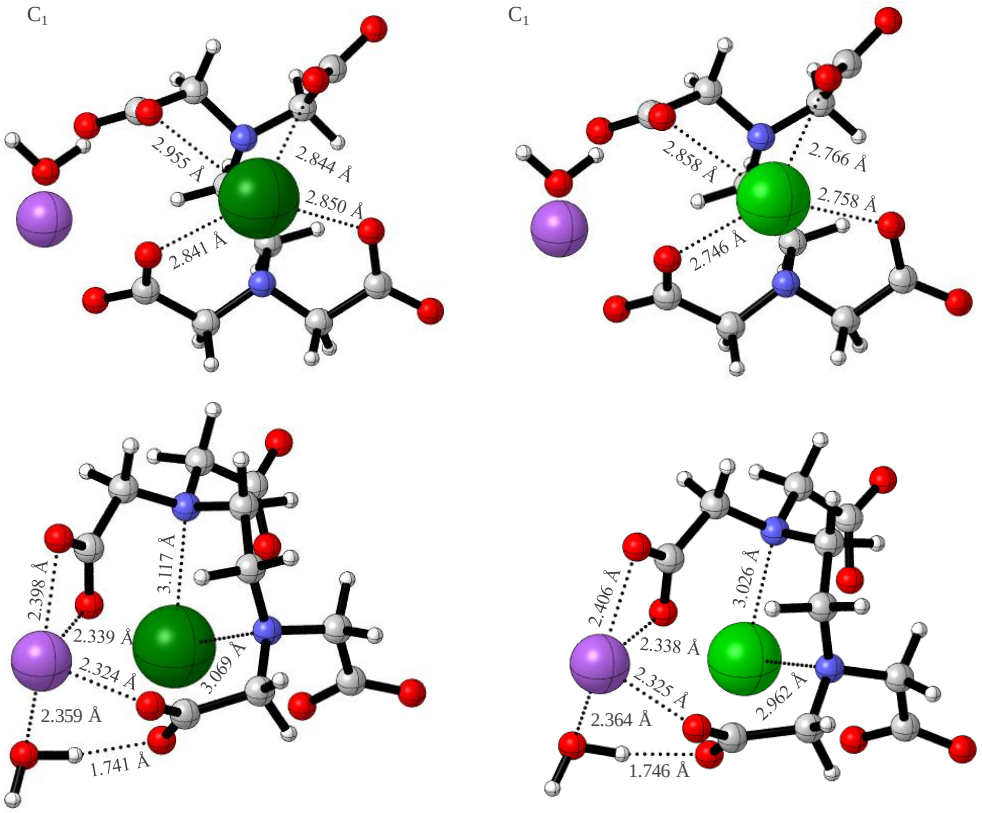


Fig. S4 Computed structure at the SMD sr-MN15/ACVDZ level of theory for the most stable conformation of $[RaEDTA(H_2O)_1Na]^-$ (left, two views) and $[BaEDTA(H_2O)_1Na]^-$ (right, two views).

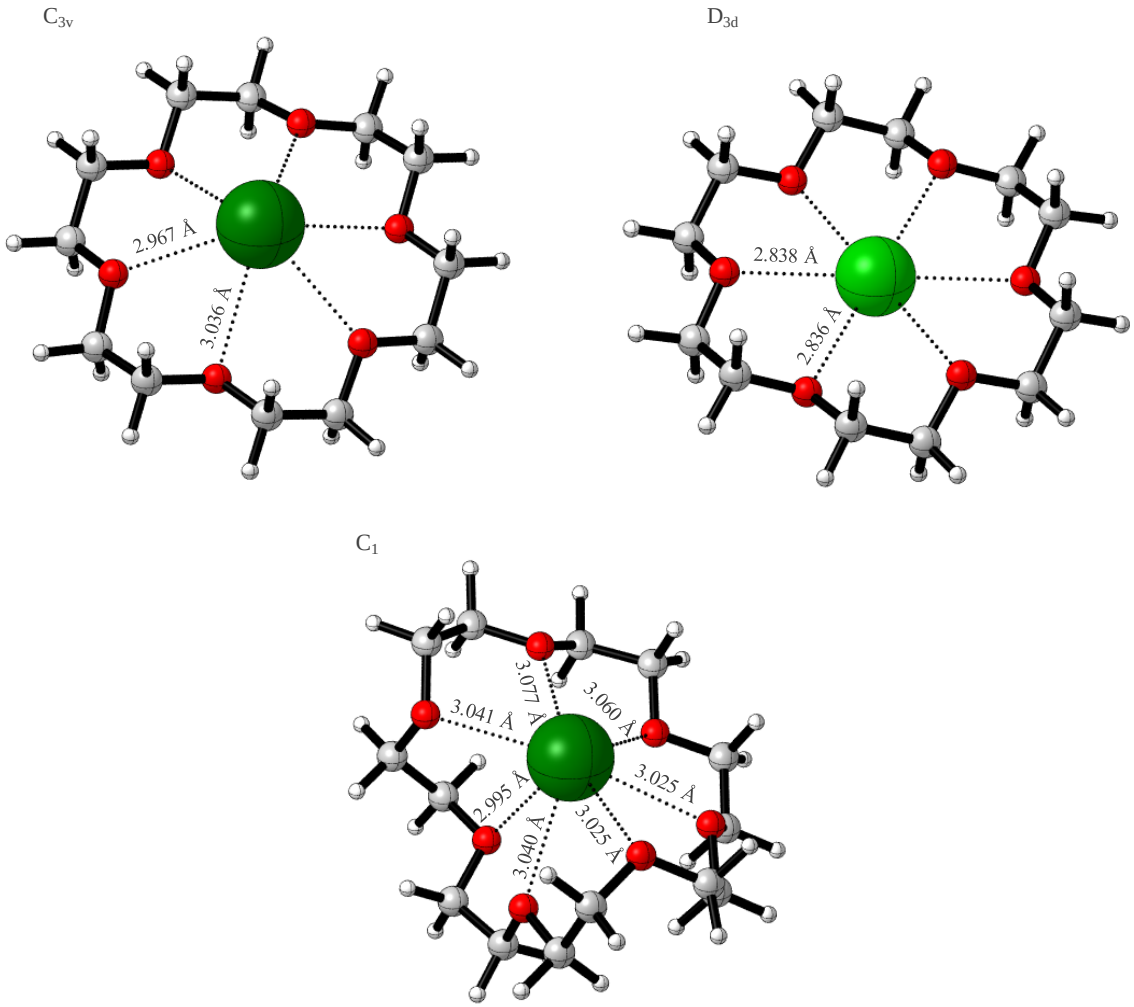


Fig. S5 Computed structure at the SMD sr-MN15/ACVDZ level of theory for the most stable conformation of $[Ra\cdots 18C6]^{2+}$ (up left), $[Ba\cdots 18C6]^{2+}$ (up right) and $[Ra\cdots 21C7]^{2+}$ (down).

II. Tables

Table S1 Absolute percentage error (APE) for computed interaction distances in reference structures using several DFT functionals and the ACVDZ set of basis function

DFT functional	$RaCO_3$	$RaSO_4$	$[RaH_2O]^{2+}$	BIWBAK			AZELOG				
	Ra–O	Ra–O	Ra–O	Ba–O_1	Ba–O_2	Ba–O_3	Ba–O_1	Ba–O_2	Ba–O_3	Ba–O_4	Ba–N
MN15	1.2	0.5	0.2	3.9	3.7	0.8	3.0	0.6	2.1	0.9	0.2
HSE03	1.4	0.8	0.0	3.0	3.0	1.5	1.3	0.1	4.0	1.3	0.4
PBE0	1.3	0.7	0.1	3.0	3.1	1.6	1.1	0.2	4.3	1.5	0.0
HSE06	1.4	0.8	0.1	3.0	3.0	1.5	1.3	0.2	4.1	1.4	0.5
PW6B95	1.4	0.7	0.5	3.2	3.3	1.2	2.3	0.7	3.2	1.2	0.1
mPW3PBE	1.4	0.8	0.3	2.7	3.3	1.8	1.0	0.4	4.6	1.7	0.6
B3PW91	1.5	0.9	0.5	2.5	3.4	1.9	0.8	0.5	4.9	1.8	0.7
TPSSh	1.8	1.0	0.3	2.6	3.3	1.9	0.8	0.5	4.5	1.5	0.6
BMK	1.1	0.9	1.0	2.2	3.7	1.8	1.0	1.0	3.6	2.4	0.6
M08-HX	1.9	1.3	0.6	3.7	3.3	0.8	2.7	0.5	2.3	1.1	0.1
τ-HCTHhyb	1.7	1.2	0.4	2.5	3.6	2.2	1.0	0.7	5.1	2.0	1.1
B98	1.7	1.3	0.8	2.1	3.9	2.4	0.3	0.8	5.5	2.3	1.2
M06-HX	1.2	0.9	0.3	3.9	3.5	0.8	5.6	0.5	5.4	0.8	2.4
B3LYP	2.2	1.7	1.1	1.8	3.8	2.4	0.0	0.8	5.3	2.3	1.3
ωB97X	1.8	1.4	0.7	2.6	3.4	1.6	7.9	0.2	7.5	1.9	1.1

Table S2 Mean absolute percentage error (MAPE) for computed interaction distances in Ra(II) complexes using the ACVDZ and ACVTZ sets of basis function

DFT functional	Ra–O	
	ACVDZ	ACVTZ
MN15	0.6	0.7
PBE0	0.7	0.7
PW6B95	0.9	0.5
M08-HX	1.3	0.2
B3LYP	1.7	0.4
ωB97X	1.3	0.1

Table S3 Computed sr-HF energies and sr-CCSD(T) correlation energies with the ACV*X*Z basis sets for $M^{2+}\cdots L$ complexes and their fragments (M = Ra, Ba; L = CO_3^{2-}, SO_4^{2-}, H_2O), at the optimized sr-CCSD(T)/ACVTZ geometries

	X	$M^{2+}\cdots L$		L		M^{2+}	
		HF (a.u.)	**corr. (a.u.)**	**HF (a.u.)**	**corr. (a.u.)**	**HF (a.u.)**	**corr. (a.u.)**
$Ra^{2+}\cdots CO_3^{2-}$	T	-286.33278	-1.21184	-262.40758	-0.99728	-23.17401	-0.19238
	Q	-286.35176	-1.35754	-262.42395	-1.11335	-23.17401	-0.22022
	5	-286.35596	-1.41402	-262.42779	-1.15849	-23.17405	-0.22935
$Ra^{2+}\cdots SO_4^{2-}$	T	-720.88003	-1.54699	-697.00524	-1.32644	-23.17401	-0.19238
	Q	-720.91809	-1.74140	-697.04122	-1.49154	-23.17401	-0.22022
	5	-720.93496	-1.92607	-697.05736	-1.66484	-23.17405	-0.22935
$Ra^{2+}\cdots H_2O$[a]	D	-99.27010	-0.34306	-76.04132	-0.23473	-23.17358	-0.10630
	T	-99.29111	-0.49322	-76.06049	-0.29704	-23.17401	-0.19238
	Q	-99.29665	-0.55399	-76.06587	-0.32939	-23.17401	-0.22022
$Ba^{2+}\cdots CO_3^{2-}$	T	-287.77220	-1.23158	-262.40758	-0.99728	-24.59335	-0.20978
	Q	-287.79117	-1.37674	-262.42395	-1.11335	-24.59336	-0.23667
	5	-287.79541	-1.43293	-262.42779	-1.15849	-24.59336	-0.24522
$Ba^{2+}\cdots SO_4^{2-}$	T	-722.31623	-1.56631	-697.00524	-1.32644	-24.59335	-0.20978
	Q	-722.35437	-1.75997	-697.04122	-1.49154	-24.59336	-0.23667
	5	-722.37128	-1.94424	-697.05736	-1.66484	-24.59336	-0.24522
$Ba^{2+}\cdots H_2O$[a]	D	-100.69393	-0.35806	-76.04132	-0.23473	-24.59293	-0.12134
	T	-100.71478	-0.51081	-76.06049	-0.29704	-24.59335	-0.20978
	Q	-100.72037	-0.57067	-76.06587	-0.32939	-24.59336	-0.23667

[a] The sr-CCSD(T) iterations failed to converge with the ACV5Z basis set. The complete basis set extrapolation was then performed using energies computed with the ACVDZ, ACVTZ and ACVQZ basis sets.

Table S4 Absolute percentage error (APE) for calculated energies of exchange reactions (1-4) using several DFT functionals and both ACVDZ and ACVTZ basis sets

DFT functional	Basis set	reactions			
		1	**2**	**3**	**4**
ωB97X	ACVDZ	5.1	10.0	10.6	6.2
	ACVTZ	0.2	2.8	2.8	2.1
M08-HX	ACVDZ	2.7	7.2	7.7	6.5
	ACVTZ	1.3	5.8	5.3	1.5
MN15	ACVDZ	8.2	8.0	10.4	8.5
	ACVTZ	3.1	6.0	4.6	1.3
PW6B95	ACVDZ	1.4	16.2	19.1	15.3
	ACVTZ	0.9	9.1	5.0	6.8
M06-2X	ACVDZ	1.0	10.8	9.7	9.0
	ACVTZ	10.2	4.7	4.4	0.9
TPSSh	ACVDZ	0.8	22.1	26.7	23.1
	ACVTZ	2.6	9.5	12.2	13.6
PBE0	ACVDZ	3.2	19.6	22.0	19.1
	ACVTZ	6.6	7.1	7.9	10.2
HSE06	ACVDZ	3.3	19.3	22.1	19.8
	ACVTZ	6.8	6.9	8.1	10.5
B98	ACVDZ	5.6	18.9	21.4	17.4
	ACVTZ	8.9	6.0	7.6	8.6
HSE03	ACVDZ	3.8	20.1	22.7	20.1
	ACVTZ	7.6	7.6	8.7	10.9
τ-HCTHhyb	ACVDZ	4.8	21.2	24.2	20.4
	ACVTZ	7.9	7.1	9.1	10.2
B3PW91	ACVDZ	4.7	21.4	24.0	19.8
	ACVTZ	7.8	8.0	9.1	10.1
mPW3PBE	ACVDZ	4.6	21.5	24.2	20.7
	ACVTZ	7.6	8.4	9.6	11.3
B3LYP	ACVDZ	6.6	21.0	24.5	43.7
	ACVTZ	9.0	9.1	11.2	13.4
BMK	ACVDZ	2.5	5.5	6.8	7.6
	ACVTZ	15.3	14.1	7.4	16.3
average	ACVDZ	6.4	16.2	18.4	17.2
	ACVTZ	3.9	7.5	7.5	8.5

Table S5 Absolute error (AE) on calculated values of log K_{exc} for the exchange reactions between Ra^{2+} and Ba^{2+}

	DFT functional	Ra Coulomb radius			
		2.115 Å	**2.110 Å**	**2.105 Å**	**2.100 Å**
L = HO^-	ωB97X	0.19	0.26	0.19	0.14
	M08-HX	0.58	0.50	0.43	0.36
	MN15	0.26	0.18	0.11	0.04
	PW6B95	0.16	0.10	0.04	0.03
L = $EDTA^{4-}$	ωB97X	0.17	0.12	0.41	0.70
	M08-HX	0.22	0.08	0.39	0.69
	MN15	0.36	0.05	0.25	0.55
	PW6B95	0.13	0.42	0.72	1.02

Table S6 Interatomic distances (Å) of the metal coordination environments for the most stable conformation of [M(macropa)(H_2O)$_n$] (M = Ba, Ra and *n* = 0-3) computed at the SMD sr-MN15/ACVDZ level of theory [a]

	M	M-N_p	M-N_p	M-O_p	M-O_p	M-O_c	M-O_c	M-O_c	M-O_c	M-N_A	M-N_A
experiment	Ba	2.933	2.929	2.784	2.808	2.881	2.847	2.884	2.833	3.015	3.006
n = 0	Ba	2.919	2.919	2.821	2.821	2.885	2.888	2.885	2.888	3.024	3.024
deviation[b]		0.5%	0.4%	1.3%	0.5%	0.2%	1.5%	0.1%	2.0%	0.3%	0.6%
	Ra	2.980	2.980	2.902	2.902	2.917	2.939	2.917	2.939	3.044	3.044
n = 3	Ba	2.909	2.915	2.827	2.852	2.900	2.900	2.940	2.901	3.010	3.011
deviation[b]		0.8%	0.5%	1.5%	1.6%	0.7%	1.9%	1.9%	2.4%	0.1%	0.2%
	Ra	2.971	2.980	2.914	2.939	2.930	2.934	2.965	2.937	3.045	3.031

[a] N_P = pyridyl nitrogen atoms, O_P = picolinate oxygen atoms, O_C = crown oxygen atoms, N_A = amine nitrogen. [b] Absolute deviation with respect to the crystallographic distance in CSD Refcode BINWUT.

III. Computed structures

Computed structures at the sr-CCSD(T)/ACVTZ level of theory.

Cartesian coordinates (in angstroms).

$RaCO_3$ (C_{2v})
C 0.000000 -0.000000 -2.141878
O 0.000000 -0.000000 -3.354718
Ra 0.000000 0.000000 0.703981
O 0.000000 1.120098 -1.391330
O -0.000000 -1.120098 -1.391330

$RaSO_4$ (C_{3v})
S 0.000000 0.000000 -1.866142
O 0.000000 0.000000 -3.303883
Ra 0.000000 0.000000 0.970227
O 0.000000 1.382477 -1.212110
O -1.197260 -0.691238 -1.212110
O 1.197260 -0.691238 -1.212110

$[RaH_2O]^{2+}$ (C_{2v})
O 0.000000 0.000000 -2.403230
Ra -0.000000 0.000000 0.286743
H 0.000000 0.758394 -3.003770
H -0.000000 -0.758394 -3.003770

$BaCO_3$ (C_{2v})
C 0.000000 0.000000 -1.829200
O 0.000000 0.000000 -3.039888
Ba -0.000000 -0.000000 0.936785
O -0.000000 1.117073 -1.072855
O -0.000000 -1.117073 -1.072855

$BaSO_4$ (C_{3v})
S 0.000000 0.000000 -1.527011
O 0.000000 0.000000 -2.963274
Ba 0.000000 0.000000 1.230808
O -0.000000 1.379600 -0.866119
O -1.194769 -0.689800 -0.866119
O 1.194769 -0.689800 -0.866119

$[BaH_2O]^{2+}$ (C_{2v})
O 0.000000 0.000000 -2.183718
Ba -0.000000 0.000000 0.411413
H -0.000000 0.759188 -2.784692
H -0.000000 -0.759188 -2.784692

Computed structure at the SMD sr-MN15/ACVDZ level of theory for the most stable conformations of [RaEDTA(H_2O)$_1$Na]$^-$.

Geometries (cartesian coordinates in angstroms) and relative stabilities in solution (ΔG^*_{298} at 2c-MN15/ACVTZ level of theory) of low-lying conformers.

1: $\Delta G^*_{298} = 0.0$ kJ mol^{-1}

O	1.948117	1.762790	-0.233529
O	3.111356	1.047509	1.550721
O	-1.493871	2.585836	-0.167935
O	-2.834888	3.422839	1.428552
O	1.800086	-1.259812	-0.326559
O	2.756775	-2.642726	1.140192
O	-2.852384	-0.555508	-0.324255
O	-4.259020	-2.290102	-0.077949
N	-0.237033	0.906307	1.626278
N	-0.731343	-2.020633	0.683705
C	2.075165	1.525228	1.011857
C	0.863343	1.848306	1.877605
H	1.141746	1.851399	2.948209
H	0.531675	2.859218	1.598700
C	-1.965478	2.608238	1.009788
C	-1.491193	1.551346	2.004553
H	-1.422356	2.013830	3.009203
H	-2.299649	0.806480	2.053982
C	-0.012992	-0.321933	2.401810
H	-0.137194	-0.114518	3.484965
H	1.036502	-0.627541	2.265842
C	-0.944233	-1.462684	2.026644
H	-0.833361	-2.263061	2.786022
H	-1.986037	-1.117806	2.091685
C	1.749439	-2.221999	0.499186
C	0.413373	-2.928567	0.677083
H	0.328438	-3.599473	-0.192991
H	0.447044	-3.561460	1.583512
C	-3.108501	-1.770643	-0.061260
C	-1.944135	-2.710252	0.255659
H	-2.290473	-3.454845	0.999359
H	-1.735009	-3.259377	-0.677061
O	4.098244	0.697239	-1.521632
H	4.817661	1.341439	-1.585224
H	3.335782	1.181903	-1.110323
Na	3.979691	-0.739136	0.345108
Ra	-0.340191	0.284407	-1.377049

2: $\Delta G^*_{298} = +8.2$ kJ mol^{-1}

O	-1.516888	-1.322509	0.043726
O	-2.229500	-2.978571	1.350151
O	2.334897	-1.850539	-1.073582
O	4.060811	-2.746802	0.049729
O	-2.074985	1.635675	-0.533036
O	-3.668569	0.995437	0.906986
O	2.183841	1.990312	-0.061894
O	2.320442	4.056171	0.807870
N	0.940132	-1.391334	1.302910
N	-0.101018	1.442108	1.446847
C	-1.302400	-2.288742	0.839373
C	0.153160	-2.614221	1.159676
H	0.201299	-3.249669	2.064997
H	0.543707	-3.203199	0.313124
C	2.954764	-2.139847	-0.004888
C	2.366380	-1.687003	1.329240
H	2.615528	-2.446578	2.097263
H	2.914838	-0.768378	1.599559
C	0.536246	-0.703769	2.537594
H	1.094082	-1.104276	3.407013
H	-0.522365	-0.935632	2.730263
C	0.719756	0.802113	2.483292
H	0.491546	1.226811	3.482803
H	1.774686	1.034619	2.271169
C	-2.483445	1.353048	0.634451
C	-1.516615	1.416319	1.807812
H	-1.796163	2.291504	2.429308
H	-1.737427	0.530223	2.416914
C	1.728729	2.956455	0.626548
C	0.341251	2.818805	1.251434
H	0.329126	3.387746	2.202947
H	-0.358297	3.323962	0.564683
O	-3.668630	-0.221176	-1.922264
H	-3.043452	-0.756853	-2.433096
H	-3.121623	0.499366	-1.529230
Na	-3.792999	-1.276990	0.263354
Ra	0.381198	0.203624	-1.321495

3: $\Delta G^*_{298} = +9.8$ kJ mol^{-1}

O	-1.516614	-1.322809	0.043641
O	-2.228998	-2.978980	1.350050
O	2.335070	-1.850261	-1.073609
O	4.060905	-2.747138	0.049411
O	-2.075640	1.635459	-0.533108
O	-3.668858	0.994776	0.907127
O	2.183228	1.991128	-0.062068
O	2.319673	4.056789	0.808196
N	0.940523	-1.391416	1.302740
N	-0.101300	1.442001	1.446683
C	-1.301990	-2.288982	0.839313
C	0.153638	-2.614356	1.159464
H	0.201882	-3.249869	2.064733
H	0.544160	-3.203239	0.312839
C	2.955250	-2.139469	-0.005057
C	2.366814	-1.686885	1.329129
H	2.616128	-2.446438	2.097129
H	2.915089	-0.768154	1.599448
C	0.536463	-0.703887	2.537366
H	1.094376	-1.104238	3.406811
H	-0.522089	-0.936039	2.730004
C	0.719619	0.802058	2.483048
H	0.491380	1.226673	3.482593
H	1.774493	1.034787	2.270891
C	-2.483843	1.352651	0.634421
C	-1.516871	1.415891	1.807677
H	-1.796547	2.290871	2.429410
H	-1.737519	0.529615	2.416574
C	1.728209	2.956945	0.626888
C	0.340665	2.818834	1.251552
H	0.328239	3.387656	2.203134
H	-0.358922	3.323872	0.564758
O	-3.669453	-0.221569	-1.922018
H	-3.044566	-0.756607	-2.433867
H	-3.122475	0.499121	-1.529198
Na	-3.792714	-1.277775	0.263082
Ra	0.381357	0.203835	-1.321351

Computed structure at the SMD sr-MN15/ACVDZ level of theory for the most stable conformations of $[Ra\cdots 18C6]^{2+}$.

Geometries (cartesian coordinates in angstroms) and relative stabilities in solution (ΔG^*_{298} at 2c-MN15/ACVTZ level of theory) of low-lying conformers.

1: $\Delta G^*_{298} = 0.0\ \text{kJ mol}^{-1}$

C 0.438008 -3.595026 -0.715252
O -2.630004 -0.853950 -0.577073
C -3.627746 0.062143 -0.139980
C -3.332499 1.416390 -0.722055
O -2.111970 1.901094 -0.176364
C -1.753142 3.165096 -0.719949
C -0.437531 3.596752 -0.134172
O 0.576681 2.698234 -0.570042
C 1.868204 3.105893 -0.132641
C 2.893801 2.175030 -0.716504
O 2.703943 0.874651 -0.173694
C 3.619410 -0.065724 -0.720837
C 3.337004 -1.422882 -0.139977
O 2.051712 -1.850445 -0.576827
C 1.757731 -3.170808 -0.134349
O -0.591712 -2.778410 -0.173193
C -1.866220 -3.105178 -0.711820
C -2.896734 -2.178577 -0.129800
H -3.632408 0.109766 0.964255
H -4.621270 -0.274286 -0.480540
H -4.155554 2.109107 -0.478023
H -3.244956 1.347338 -1.820554
H -2.526975 3.912968 -0.477609
H -1.672121 3.086297 -1.818233
H 1.912067 3.085081 0.971563
H 2.072377 4.135085 -0.472389
H 3.904911 2.541685 -0.471293
H 2.790647 2.135902 -1.815081
H 4.653915 0.230157 -0.477563
H 3.510254 -0.091794 -1.819162
H 3.361790 -1.382589 0.964330
H 4.106525 -2.134928 -0.482311
H -2.125388 -4.147456 -0.460020
H -1.840704 -3.004448 -1.811055
H -2.866165 -2.212658 0.974602
H -3.900468 -2.492328 -0.462222
H 0.454301 -3.489840 -1.814174
H 0.250060 -4.653100 -0.466155
H -0.487826 3.595991 0.969924
H -0.203838 4.619837 -0.473568
H 2.545707 -3.864727 -0.472087
H 1.718718 -3.194754 0.970064
Ra 0.000063 0.002337 0.675442

2: $\Delta G^*_{298} = +2.6\ \text{kJ mol}^{-1}$

O -2.495697 0.879476 0.000000
O -1.291422 0.207200 2.485723
O -1.291422 0.207200 -2.485723
C -3.244762 0.593910 1.176307
H -3.466472 -0.487701 1.224496
H -4.199155 1.146417 1.154558
C -2.452539 1.020103 2.380407
H -2.156788 2.079902 2.287047
H -3.074313 0.907812 3.284782
C -0.488146 0.568666 3.600933
C -0.488146 0.568666 -3.600933
H -0.212477 1.635360 -3.528442
H -1.052846 0.426232 -4.538744
C -2.452539 1.020103 -2.380407
H -3.074313 0.907812 -3.284782
H -2.156788 2.079902 -2.287047
C -3.244762 0.593910 -1.176307
H -4.199155 1.146417 -1.154558
H -3.466472 -0.487701 -1.224496
C 0.729748 -0.322761 -3.618961
O 1.517013 -0.198171 -2.438243
C 2.284912 0.999048 -2.381179
C 3.180086 0.932801 -1.175541
O 2.379966 0.959555 -0.000000
C 3.180086 0.932801 1.175541
C 2.284912 0.999048 2.381179
O 1.517013 -0.198171 2.438243
C 0.729748 -0.322761 3.618961
H 1.628122 1.881948 -2.309286
H 2.901516 1.088749 -3.291138
H 3.865574 1.797365 -1.181177
H 3.782489 0.007382 -1.195371
H 3.865574 1.797365 1.181177
H 3.782489 0.007382 1.195371
H 1.628122 1.881948 2.309286
H 2.901516 1.088749 3.291138
H -0.212477 1.635360 3.528442
H -1.052846 0.426232 4.538744
H 0.413842 -1.374884 -3.666463
H 1.341412 -0.094054 -4.507546
H 1.341412 -0.094054 4.507546
H 0.413842 -1.374884 3.666463
Ra -0.026557 -0.890761 0.000000

3: $\Delta G^*_{298} = +3.0\ \text{kJ mol}^{-1}$

O -2.526653 1.154699 0.146197
O -0.142077 2.586812 0.774392
O 2.402169 1.485475 0.235549
O 2.487041 -1.306108 0.576090
O 0.093097 -2.574299 0.566416
O -2.372276 -1.659548 -0.165333
C -2.516292 2.371055 0.883711
H -2.423923 2.150753 1.961715
H -3.460149 2.917010 0.716350
C -1.366371 3.222064 0.422859
H -1.410644 3.366309 -0.672049
H -1.427475 4.210444 0.908461
C 0.981805 3.387558 0.421964
H 0.891119 4.384486 0.884903
H 1.018942 3.512609 -0.675590
C 2.235641 2.721564 0.916337
H 3.098773 3.380625 0.722212
H 2.169609 2.538895 2.003231
C 3.576147 0.797552 0.648098
H 3.587168 0.712311 1.748772
H 4.473659 1.353375 0.328705
C 3.574822 -0.572829 0.028479
H 3.459433 -0.497984 -1.069279
H 4.528075 -1.082433 0.247096
C 2.402189 -2.626838 0.055757
H 3.348140 -3.168814 0.221305
H 2.207515 -2.582114 -1.032580
C 1.276446 -3.334820 0.761392
H 1.158723 -4.348799 0.344046
H 1.485401 -3.417602 1.842220
C -1.071195 -3.191991 1.096076
H -0.873427 -3.565557 2.114804
H -1.367680 -4.040915 0.456218
C -2.159428 -2.153390 1.153681
H -3.085921 -2.604182 1.546972
H -1.848316 -1.331327 1.822795
C -3.586025 -0.931092 -0.322842
H -4.445765 -1.566380 -0.050180
H -3.651407 -0.681780 -1.391321
C -3.630458 0.332861 0.502286
H -4.578016 0.858899 0.292983
H -3.596995 0.115022 1.584164
Ra 0.033057 0.020008 -0.810559

Computed structure at the SMD sr-MN15/ACVDZ level of theory for the most stable conformations of $[Ra\cdots 21C7]^{2+}$.

Geometries (cartesian coordinates in angstroms) and relative stabilities in solution (ΔG^*_{298} at 2c-MN15/ACVTZ level of theory) of low-lying conformers.

1: $\Delta G^*_{298} = +0.0\ \mathrm{kJ\ mol^{-1}}$

O	1.968393	1.748052	0.548880
O	2.976279	-0.103398	-1.289031
O	1.805552	-1.960689	0.529522
C	1.745065	1.997101	1.931159
H	2.352154	2.854683	2.266044
H	2.032496	1.108750	2.522785
C	3.343617	1.803112	0.193071
H	3.949178	1.243601	0.927006
H	3.697307	2.848520	0.191527
C	3.490787	1.221827	-1.192898
H	2.907771	1.820671	-1.908478
H	4.551549	1.244053	-1.492448
C	3.723859	-1.102079	-0.600133
H	4.764467	-0.768587	-0.456659
H	3.731744	-1.996132	-1.241700
C	3.121780	-1.464213	0.737073
H	3.744599	-2.247459	1.204787
H	3.084973	-0.602286	1.424177
C	1.203352	-2.373665	1.751102
O	-1.040366	-2.154349	0.956539
C	-2.165780	-2.814192	0.383581
C	-3.305200	-1.839586	0.279902
O	-2.914706	-0.746737	-0.538454
C	-3.912723	0.262370	-0.586020
C	-3.306729	1.516190	-1.168197
O	-2.181762	1.972793	-0.419854
C	-2.467369	2.401882	0.910576
C	-1.898564	1.425795	1.922702
O	-0.499469	1.213998	1.742430
C	0.292929	2.331459	2.130352
H	-2.478922	-3.654105	1.025802
H	-1.893344	-3.213424	-0.609470
H	-3.573791	-1.465477	1.284678
H	-4.185922	-2.346770	-0.149548
H	-4.293578	0.448102	0.434513
H	-4.763555	-0.061157	-1.210012
H	-4.077126	2.302821	-1.225645
H	-2.930717	1.316238	-2.182918
H	-3.553419	2.494758	1.069067
H	-2.029532	3.402823	1.040245
H	-2.370527	0.438332	1.811770
H	-2.092584	1.799157	2.943342
C	-0.081116	-3.088255	1.441048
H	1.880258	-3.061403	2.285444
H	1.016219	-1.493681	2.395173
H	0.039457	3.214780	1.522060
H	0.109438	2.568153	3.191992
H	-0.465871	-3.578913	2.350678
H	0.104837	-3.862151	0.676087
Ra	0.012814	-0.024747	-0.921937

2: $\Delta G^*_{298} = +2.5\ \mathrm{kJ\ mol^{-1}}$

O	0.197831	2.265407	1.353061
O	-2.248156	1.592988	0.265562
O	2.504708	1.561933	-0.098637
C	-0.880339	1.850944	2.182439
H	-0.805437	2.327617	3.174203
H	-0.835335	0.751304	2.315877
C	-2.181502	2.231276	1.531436
H	-3.011826	1.885794	2.171460
H	-2.261129	3.324968	1.407185
C	-3.560897	1.542493	-0.269052
C	3.768787	1.252547	-0.666215
H	4.487809	1.036770	0.142241
H	4.164525	2.095952	-1.256436
C	2.563574	2.406956	1.043977
H	2.482024	3.464420	0.741397
H	3.522755	2.261775	1.567394
C	1.450954	2.026250	1.982336
H	1.534617	0.950884	2.235244
H	1.524885	2.614833	2.912535
C	3.585963	0.051735	-1.571693
O	2.834157	-0.985213	-0.948731
C	3.361133	-1.444099	0.289860
C	2.463025	-2.536803	0.798012
O	1.187781	-1.980853	1.103548
C	0.315628	-2.967732	1.641815
C	-1.033717	-2.362790	1.909329
O	-1.633022	-2.001419	0.671470
C	-2.978146	-1.562811	0.828513
C	-3.596606	-1.441454	-0.545514
O	-2.890486	-0.525850	-1.379893
C	-3.507667	0.747020	-1.552398
H	3.386712	-0.624707	1.029461
H	4.383618	-1.833551	0.151109
H	2.903182	-2.982121	1.706210
H	2.348469	-3.329539	0.038107
H	0.733372	-3.360664	2.584342
H	0.218967	-3.804023	0.927124
H	-0.939786	-1.475340	2.561042
H	-1.663431	-3.107297	2.425459
H	-2.998776	-0.608119	1.384101
H	-3.547615	-2.311879	1.406275
H	-4.653085	-1.143017	-0.452998
H	-3.556804	-2.424034	-1.039575
H	-4.239914	1.074268	0.466764
H	-3.937270	2.557417	-0.483641
Ra	0.026683	0.029120	-0.827941
H	4.575922	-0.319153	-1.887071
H	3.011573	0.331732	-2.467243
H	-2.892292	1.276269	-2.295163
H	-4.527459	0.629737	-1.954722

3: $\Delta G^*_{298} = +2.8\ \mathrm{kJ\ mol^{-1}}$

O	-2.153654	-1.816572	0.264022
C	-3.510252	-1.462108	0.020450
C	-3.610934	-0.801042	-1.332356
O	-2.899151	0.434617	-1.370801
C	-3.544951	1.502898	-0.678859
C	-1.307509	1.880628	2.174774
C	-0.162843	2.804356	1.842555
C	1.879926	2.911133	0.675328
C	3.135336	2.114766	0.455129
C	4.016022	0.240089	-0.662975
C	3.553740	-1.075898	-1.244525
C	1.693426	-2.683128	1.484602
O	0.436729	-2.023702	1.377658
C	-0.630245	-2.879533	1.765576
C	-1.938338	-2.152839	1.630014
H	-3.859294	-0.778511	0.814448
H	-4.145205	-2.364559	0.041775
H	-4.670157	-0.645432	-1.593608
H	-3.153384	-1.446468	-2.096407
H	-4.325888	1.106139	-0.012353
H	-4.015637	2.187716	-1.401618
H	-0.944898	1.037473	2.781789
H	-2.062710	2.439697	2.753098
H	0.217156	3.258514	2.773723
H	-0.495590	3.621379	1.178607
H	2.102845	3.721855	1.388543
H	1.524257	3.361001	-0.268580
H	3.462430	1.661098	1.408468
H	3.933270	2.784213	0.091212
H	4.508328	0.085408	0.312391
H	4.752047	0.703543	-1.341301
H	4.411779	-1.767698	-1.294056
H	3.155090	-0.929858	-2.258923
H	1.920753	-2.891900	2.543493
H	1.653845	-3.640167	0.936014
H	-0.496799	-3.195035	2.814425
H	-0.628055	-3.779651	1.125975
H	-1.944555	-1.233947	2.245022
H	-2.743600	-2.816986	1.985976
O	-1.909821	1.303842	1.020898
O	0.870061	2.058674	1.208819
O	2.885464	1.083005	-0.488936

O 2.490681 -1.656317 -0.492764
C 2.755963 -1.796501 0.898846
C -2.515932 2.243922 0.136522
Ra 0.039511 -0.037616 -0.826166
H -3.002051 3.053392 0.706135
H -1.752748 2.691371 -0.527256
H 3.747175 -2.252789 1.058055
H 2.731645 -0.808445 1.395905

4: $\Delta G^*_{298} = +3.9$ kJ mol^{-1}
O 2.278534 1.815643 0.054357
O -0.216247 2.429562 1.229425
O -2.531728 1.650210 -0.225336
O -2.780890 -1.059590 -0.941396
O -1.190611 -2.304310 1.006443
O 1.612649 -2.363782 0.569098
O 2.841621 -0.620983 -1.334184
C 2.180386 2.369457 1.361569
H 3.055312 3.006362 1.571422
H 2.148397 1.557166 2.110399
C 0.946344 3.225219 1.432583
H 0.894134 3.719948 2.417459
H 0.994446 4.004896 0.651933
C -1.368305 3.256316 1.112135
H -1.256309 3.915958 0.233495
H -1.466383 3.889038 2.011044
C -2.606649 2.417026 0.971634
H -2.726915 1.740530 1.836557
H -3.475371 3.095104 0.932572
C -3.801340 1.133933 -0.608236
H -4.387816 1.905848 -1.134820
H -4.368027 0.837020 0.290033
C -3.588568 -0.043779 -1.529739
H -4.569098 -0.457130 -1.821680
H -3.053542 0.277441 -2.435291
C -3.329540 -1.624458 0.244147
H -4.364563 -1.958754 0.060872
H -3.331932 -0.883041 1.062008
C -2.476614 -2.793731 0.649141
H -2.938416 -3.302257 1.512373
H -2.385297 -3.517150 -0.179864
C -0.347057 -3.334756 1.502026
H -0.259867 -4.139929 0.751350
H -0.775979 -3.760579 2.424984
C 1.006615 -2.752738 1.795874
H 0.909521 -1.874149 2.460144
H 1.632644 -3.507195 2.301401
C 2.914022 -1.826162 0.771719
H 3.526679 -2.537729 1.352444
H 2.837836 -0.880303 1.342297
C 3.553445 -1.597289 -0.574621
H 4.599626 -1.283918 -0.433591
H 3.547639 -2.539748 -1.144052
C 3.547516 0.600403 -1.541437
H 3.000904 1.143427 -2.326560
H 4.568983 0.393769 -1.899769
C 3.606723 1.443117 -0.291634
H 4.072842 0.881870 0.537345
H 4.215371 2.344266 -0.479642
Ra -0.024697 -0.014547 -0.552762

5: $\Delta G^*_{298} = +5.5$ kJ mol^{-1}
O -2.707896 -0.716820 1.279412
C -3.268623 0.517808 1.718502
C -3.410133 1.522100 0.598164
O -2.155800 1.631841 -0.057282
C -2.191215 2.483063 -1.194041
C -1.306396 -3.003253 -1.048799
O -1.587396 -1.612302 -1.183451
C -2.974517 -1.301099 -1.074972
C -3.494340 -1.452017 0.344179
H -2.575176 0.902236 2.481885
H -4.252687 0.351136 2.186892
H -3.722211 2.493857 1.017430
H -4.176783 1.202803 -0.130923
H -2.104332 3.536390 -0.876165
H -3.149376 2.363111 -1.728417
H -3.557191 -1.963732 -1.738786
H -3.084579 -0.268195 -1.431947
H -3.460890 -2.507224 0.653970
H -4.547128 -1.127213 0.381210
C 3.783539 0.138405 0.725632
H 4.835813 -0.187377 0.776660
H 3.353936 0.093185 1.744450
C 3.716647 1.538492 0.177652
H 4.328078 2.216357 0.796079
H 4.108435 1.549800 -0.853838
C 2.121260 3.075797 -0.674046
H 2.620405 2.912186 -1.644539
H 2.521304 3.997103 -0.218776
C 0.635188 3.201636 -0.883020
H 0.121257 3.355202 0.083306
H 0.426433 4.062960 -1.538903
C 2.355768 -2.890439 -0.783880
H 2.594555 -2.614285 -1.825825
H 2.560100 -3.965990 -0.649001
C 3.201909 -2.089379 0.167325
H 2.884849 -2.275527 1.210276
H 4.259480 -2.384158 0.063766
H -1.458246 -3.331072 -0.006184
H -1.978061 -3.582926 -1.704020
C -1.077161 2.077034 -2.132487
C 0.120499 -3.256244 -1.452117
O 0.984714 -2.620707 -0.518718
O 3.044931 -0.710598 -0.145586
O 2.357617 1.954704 0.167486
O 0.188988 1.991737 -1.489064
Ra 0.168897 -0.047710 0.693432
H -1.031569 2.791559 -2.972132
H -1.274952 1.069466 -2.528503
H 0.307726 -4.343518 -1.455456
H 0.312094 -2.861947 -2.465432

6: $\Delta G^*_{298} = +6.5$ kJ mol^{-1}
O -3.014318 -0.960524 0.139231
C -3.853016 0.005294 0.759908
C -3.826439 1.258455 -0.067836
O -2.534697 1.848460 0.015650
C -2.399231 2.928227 -0.899863
C -1.160927 3.711828 -0.571933
O -0.007775 2.898820 -0.751924
C 1.175183 3.656681 -0.530900
C 2.381620 2.765798 -0.617599
O 2.332937 1.812460 0.437566
C 3.611041 1.252362 0.712502
C 3.426444 0.061137 1.618416
O 2.710185 -0.985805 0.967696
C 3.465727 -1.689100 -0.017456
C 2.765915 -1.595481 -1.356191
O 1.404725 -2.010352 -1.290466
C 1.226466 -3.360134 -0.877637
C -0.233117 -3.697419 -0.992965
O -0.956225 -2.876397 -0.085609
C -2.332877 -3.225589 -0.044684
C -3.068254 -2.220404 0.795889
H -3.499373 0.211004 1.786572
H -4.886657 -0.375896 0.815162
H -4.585842 1.967704 0.302414
H -4.057389 1.013610 -1.119506
H -3.270395 3.600124 -0.817797
H -2.354710 2.538505 -1.932145
H -1.200585 4.069014 0.472337
H -1.105793 4.590116 -1.237894
H 1.130128 4.125627 0.468036
H 1.253168 4.455845 -1.287905
H 3.283019 3.392884 -0.517919
H 2.422276 2.244691 -1.591272
H 4.253770 2.002731 1.204121
H 4.097618 0.948677 -0.231969
H 2.828854 0.350832 2.495254
H 4.407526 -0.301716 1.964736
H 3.582313 -2.734863 0.306964
H 4.475364 -1.262193 -0.120883
H 3.311375 -2.197797 -2.103639
H 2.740382 -0.544611 -1.687631
H 1.545530 -3.490516 0.170081
H 1.819140 -4.034956 -1.518193
H -0.382252 -4.761273 -0.741442
H -0.594999 -3.524044 -2.021616
H -2.454371 -4.233841 0.386450
H -2.745124 -3.229497 -1.069089
H -2.612031 -2.143241 1.799669
H -4.117699 -2.539514 0.911641
Ra -0.111740 0.033402 0.250005

Computed structure at the SMD sr-MN15/ACVDZ level of theory for the most stable conformations of Ra(macropa).

Geometries (cartesian coordinates in angstroms) and relative stabilities in solution (ΔG^*_{298} at 2c-MN15/ACVTZ level of theory) of low-lying conformers.

1: $\Delta G^*_{298} = +0.0\ \mathrm{kJ\ mol^{-1}}$

O	1.449069	-2.386788	1.715788
O	2.569142	0.273600	2.153397
O	-1.449069	2.386788	1.715788
O	-2.569142	-0.273600	2.153397
O	2.229097	-0.419992	-1.011815
O	2.543960	-0.058349	-3.208235
O	-2.229097	0.419992	-1.011815
O	-2.543960	0.058349	-3.208235
N	-1.440818	-2.681389	0.745774
N	1.440818	2.681389	0.745774
N	-0.000000	-1.876737	-1.516873
N	0.000000	1.876737	-1.516873
C	-0.462532	-3.721662	1.104423
H	0.132261	-3.965462	0.210954
H	-0.988390	-4.649500	1.407525
C	0.499896	-3.332367	2.207115
H	-0.027104	-2.898031	3.076102
H	1.033188	-4.234185	2.553374
C	2.414639	-2.049168	2.707632
H	3.028832	-2.934865	2.943356
H	1.900216	-1.727277	3.631045
C	3.307618	-0.941766	2.210419
H	4.156526	-0.827728	2.906207
H	3.707668	-1.187841	1.210192
C	3.358627	1.373549	1.710463
H	3.758285	1.157827	0.703783
H	4.217989	1.501927	2.391332
C	2.527609	2.641013	1.735803
H	2.088982	2.730879	2.740588
H	3.207132	3.506923	1.599351
C	0.462532	3.721662	1.104423
H	-0.132261	3.965462	0.210954
H	0.988390	4.649500	1.407525
C	-0.499896	3.332367	2.207115
H	0.027104	2.898031	3.076102
H	-1.033188	4.234185	2.553374
C	-2.414639	2.049168	2.707632
H	-3.028832	2.934865	2.943356
H	-1.900216	1.727277	3.631045
C	-3.307618	0.941766	2.210419
H	-4.156526	0.827728	2.906207
H	-3.707668	1.187841	1.210192
C	-3.358627	-1.373549	1.710463
H	-3.758285	-1.157827	0.703783
H	-4.217989	-1.501927	2.391332
C	-2.527609	-2.641013	1.735803
H	-2.088982	-2.730879	2.740588
H	-3.207132	-3.506923	1.599351
C	-1.985217	-2.971521	-0.578951
H	-2.881211	-2.350353	-0.740256
H	-2.325337	-4.025576	-0.646349
C	-1.044758	-2.683311	-1.728286
C	-1.322108	-3.210490	-2.998057
H	-2.165578	-3.890824	-3.128884
C	-0.520360	-2.837134	-4.072017
H	-0.722073	-3.223582	-5.072464
C	0.544741	-1.958395	-3.853338
H	1.193939	-1.632218	-4.665430
C	0.779638	-1.517444	-2.552196
C	1.946238	-0.590504	-2.234888
C	1.985217	2.971521	-0.578951
H	2.881211	2.350353	-0.740256
H	2.325337	4.025576	-0.646349
C	1.044758	2.683311	-1.728286
C	1.322108	3.210490	-2.998057
H	2.165578	3.890824	-3.128884
C	0.520360	2.837134	-4.072017
H	0.722073	3.223582	-5.072464
C	-0.544741	1.958395	-3.853338
H	-1.193939	1.632218	-4.665430
C	-0.779638	1.517444	-2.552196
C	-1.946238	0.590504	-2.234888
Ra	-0.000000	0.000000	0.798533

2: $\Delta G^*_{298} = +16.8\ \mathrm{kJ\ mol^{-1}}$

O	-0.435769	2.010571	1.765076
O	-1.932022	3.678527	1.945481
O	0.833829	-1.597906	2.032814
O	2.598943	-2.844673	2.654126
N	-2.395998	0.159365	1.655585
N	2.479197	0.423642	1.264139
C	-2.860893	-2.184446	1.321521
H	-2.103721	-2.414005	2.086864
H	-3.697877	-2.899672	1.440466
C	-3.350060	-0.776743	1.550468
C	-4.709115	-0.456537	1.614876
H	-5.456453	-1.247757	1.532788
C	-5.080038	0.879973	1.767291
H	-6.133741	1.159787	1.813706
C	-4.084569	1.852950	1.846826
H	-4.325104	2.910329	1.952744
C	-2.748732	1.445207	1.789245
C	-1.616246	2.462759	1.843026
C	2.645386	2.533182	0.074720
H	1.816208	3.003715	0.626771
H	3.404530	3.315336	-0.124691
C	3.261022	1.464308	0.942293
C	4.595870	1.539072	1.352740
H	5.196710	2.410148	1.086714
C	5.139729	0.472566	2.067482
H	6.182084	0.496814	2.389283
C	4.339652	-0.636350	2.343991
H	4.729697	-1.502514	2.877424
C	3.003301	-0.611520	1.936134
C	2.072234	-1.781293	2.232993
C	1.582731	-3.082128	-1.942892
C	-3.211227	-2.176377	-1.084165
C	-2.848469	-1.140367	-2.128207
O	-2.757435	0.146716	-1.518145
C	-2.837150	1.211264	-2.463510
C	-2.163482	2.437599	-1.904565
O	-0.758542	2.217269	-1.926977
C	0.007150	3.337682	-1.490123
C	1.445235	3.114262	-1.906668
C	3.171719	1.430807	-2.034857
C	3.566145	-0.002578	-1.725573
O	2.420843	-0.842684	-1.808074
C	2.757749	-2.207767	-1.597197
O	0.545540	-2.882772	-0.992832
C	-0.561919	-3.750285	-1.211617
C	-1.531895	-3.618915	-0.059704
H	-4.188799	-1.897995	-0.658623
H	-3.357643	-3.141510	-1.600477
H	-3.631664	-1.130462	-2.905185
H	-1.882992	-1.380071	-2.615931
H	-3.893367	1.429031	-2.691908
H	-2.326423	0.921436	-3.397976
H	-0.100849	3.467254	-0.397762
H	-0.369562	4.250719	-1.982219
H	2.006888	4.060622	-1.782046
H	1.434783	2.879764	-2.980459
H	4.090161	2.052833	-2.009102
H	2.805712	1.437797	-3.071727
H	4.051325	-0.131462	-0.743699
H	4.300397	-0.316326	-2.489181
H	-0.201475	-4.792425	-1.255662
H	-1.037040	-3.518265	-2.181879
H	-0.963538	-3.750807	0.874624
H	-2.263159	-4.449680	-0.126575
H	1.216423	-2.845290	-2.957936
H	1.903123	-4.137927	-1.924771
H	-2.509942	2.635294	-0.872408
H	-2.413586	3.312203	-2.528847
H	3.608399	-2.484413	-2.243255
H	3.056228	-2.363431	-0.541982
N	-2.222435	-2.324124	0.002382

N 2.112481 2.010252 -1.193565
Ra -0.031662 -0.077743 -0.235407