Electronic Supplementary Material for PCCP

Electronic Supplementary Information

Density Functional Studies of Model Cerium Oxide Nanoparticles

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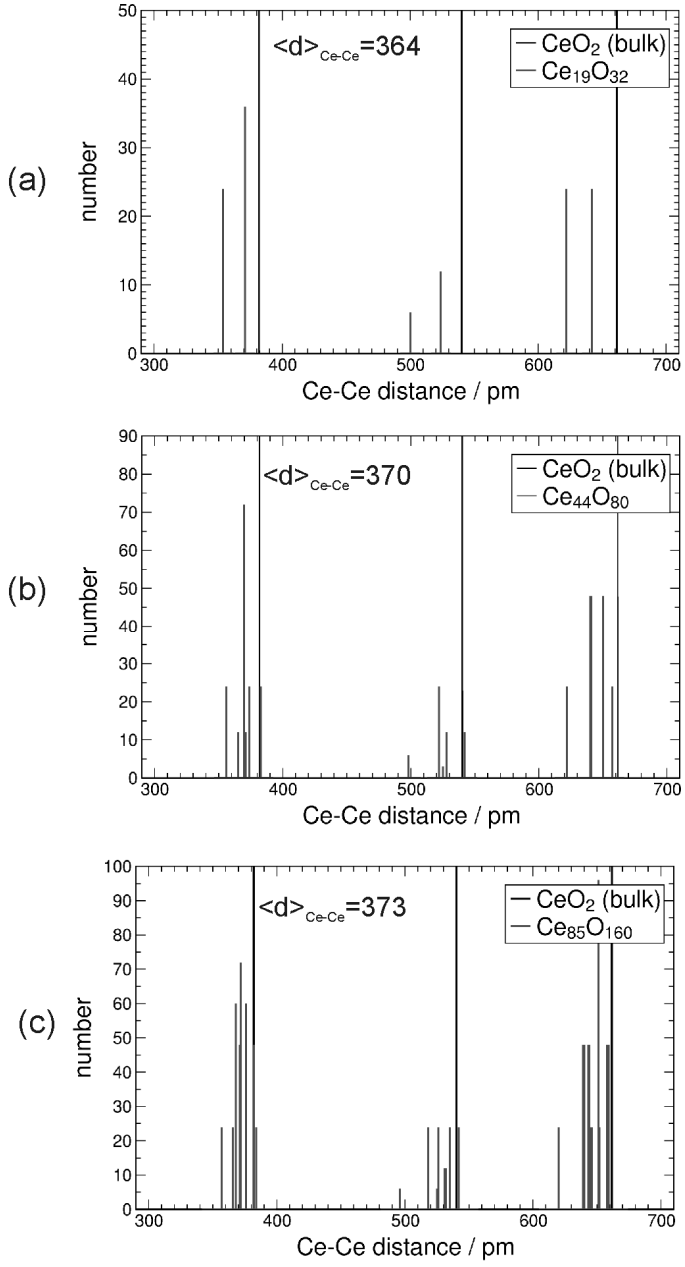

Fig. S1 Pair distribution functions of Ce-Ce distances up to 0.7 nm in octahedral clusters (grey lines) a) $Ce_{19}O_{32}$ (**b1**), b) $Ce_{44}O_{80}$ (**c1**) and c) $Ce_{85}O_{160}$ (**d1**). Average Ce-Ce distances $\langle d \rangle$ for the nearest atoms are 364, 370 and 373 pm, respectively. The values calculated for CeO_2 bulk are also shown in the panels a, b and c (black lines).

Table S1. Bond length (*d*), dissociation energy (D_0, zero-point corrected) and vibrational frequency of the CeO molecule in its triplet state (ω). PAW calculations from this work. Experimental data from CRC Handbook of Chemistry and Physics, D.R. Lide, (ed.), CRC Press, Boca Raton, Florida, USA, 81st edition, 2000.

	d / pm	D_0 / eV	ω / cm^{-1}
LDA+U	1.846	9.65	850
PW91+U	1.845	8.78	836
Exp.	1.820	8.19	834

Table S2. Calculated total energies of selected reference systems (eV). For $Ce_{(g)}$, the ^{3}G-like state of the $4f5d6s^2$ configuration is calculated, which according to J-averaged experimental data is ~0.25 eV over the multi-configurational ^{1}G ground state [M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys*., 1989, **90**, 1730.]. Note, that solid Ce has been calculated at the LDA+U (U_{eff} = 5 eV) and the GGA+U (U_{eff} = 3 eV) levels of theory.

System	*E*(LDA+U)	*E*(PW91+U)
$Ce_{(s)}$	-5.59725	-5.09685
$Ce_{(g)}$	-0.45200	-0.90312
O_2	-10.5224	-9.82229
O (^{3}P)	-1.496786	-1.75612

Table S3. Calculated cohesive (E_c, reference are reactants in atomic gas phase states) and formation energies (E_f, reference are reactants in their respective ground states) as well as averaged nearest interatomic distances <*d*> of the ceria bulk and nanoparticles: structures optimized at the LDA+U level (U_{eff} = 5 eV), energies at the LDA+U (U_{eff}=5 eV) and GGA+U (PW91, U_{eff}=3 eV) levels of theory. E_f was calculated with respect to: Ce(s) + 0.5(m/n) O_2(g) → 1/n Ce_nO_m. E_c(exp.) for CeO_2 and Ce_2O_3 was obtained from the corresponding Born-Haber cycle: E_c(exp.) = E_f(exp.) – E_{subl}(exp.) – D_{O2}(exp.). For the CeO molecule E_c corresponds to the atomization energy. E_f(exp.) for CeO molecule was calculated as: E_f(exp.) = D_{CeO}(exp.) + E_{subl}(exp.) + 0.5D_{O2}(exp.), E_{subl}(exp.) is the experimental energy of sublimation of metallic Ce at 298 K [C. E. Habermann and A. H. Daane, *J. Chem. Phys.*, 1964, **41**, 2818]. For clusters, E_c values shown are estimated upper limits - the unknown *exact* groundstates of the clusters might be very slightly lower in energy.

System	Label	<*N*>	Ce^{+3}/Ce^{+4}	<d_{Ce-Ce}>	<d_{Ce-O}>	E_c(LDA+U)	E_c(PW91+U)	E_c(exp.)	E_f(LDA+U)	E_f(PW91+U)	E_f(exp.)
				pm	pm	eV	eV	eV	eV	eV	eV
CeO_2	bulk	8.00	0/1	381.8	233.8	-23.53	-20.85	-21.24	-10.86	-10.34	-11.14
Ce_2O_3	bulk	(7)	2/0	378.5	246.0	-40.22	-35.33	-36.00	-18.63	-17.47	-18.56
Ce_6O_8	**a1**	4.00	-	342.8	225.3	-100	-89		-6.52	-6.46	
$Ce_{19}O_{32}$	**b1**	5.47	12/7	364.0	228.3	-378	-338		-8.42	-8.27	
$Ce_{44}O_{80}$	**c1**	6.18	16/28	370.0	229.4	-932	-831		-9.17	-8.95	
$Ce_{85}O_{160}$	**d1**	6.49	20/65	372.6	229.9	-1855	-1650		-9.60	-9.28	
$Ce_{13}O_{32}$	**b2**	6.15	-	370.3	222.5	-	-256		-	-7.71	
$Ce_{13}O_{26}$	**b3**	5.15	0/13	363.2	222.8	-	-247		-	-8.53	
$Ce_{13}O_{20}$	**b4**	4.30	12/1	379.1	225.7	-	-210		-	-7.10	
$Ce_{38}O_{80}$	**c2**	6.53	-	372.5	227.1	-	-756		-	-9.05	
$Ce_{38}O_{74}$	**c3**	6.26	4/34	373.9	229.3	-	-738		-	-9.09	
$Ce_{38}O_{68}$	**c4**	5.90	16/22	375.3	229.5	-	-706		-	-8.74	
CeO	molec.	1.00	-	-	184.6	-9.70	-8.83	-8.19	-0.79	-1.48	-0.79

Table S4. Cartesian atomic coordinates (Å) of the cluster $Ce_{19}O_{32}$ (**b1**) optimised at the spin-restricted (SR) LDA+U level; the state corresponds to the lowest calculated spin-polarized (SP) single-point LDA+U energy for the optimal SR geometry (SP//SR), -434.73 eV.

Ce1	11.19377	11.19377	16.51912
Ce2	13.81520	11.19377	14.14186
Ce3	8.57234	11.19377	14.14186
Ce4	11.19377	13.81520	14.14186
Ce5	11.19377	8.57234	14.14186
Ce6	13.81520	13.81520	11.52045
Ce7	13.81520	8.57234	11.52045
Ce8	8.57234	13.81520	11.52045
Ce9	8.57234	8.57234	11.52045
Ce10	16.19244	11.19377	11.52045
Ce11	11.19377	16.19244	11.52045
Ce12	11.19377	11.19377	11.52045
Ce13	11.19377	6.19508	11.52045
Ce14	6.19508	11.19377	11.52045
Ce15	13.81520	11.19377	8.89902
Ce16	8.57234	11.19377	8.89902
Ce17	11.19377	13.81520	8.89902
Ce18	11.19377	8.57234	8.89902
Ce19	11.19377	11.19377	6.52177
O1	9.80842	9.80842	15.57467
O2	12.57912	9.80842	15.57467
O3	9.80842	12.57912	15.57467
O4	12.57912	12.57912	15.57467
O5	15.24798	9.80842	12.90581
O6	9.80842	15.24798	12.90581
O7	9.85184	9.85184	12.86236
O8	15.24798	12.57912	12.90581
O9	9.85184	12.53570	12.86236
O10	9.80842	7.13956	12.90581
O11	12.57912	15.24798	12.90581
O12	12.53570	9.85184	12.86236
O13	7.13956	9.80842	12.90581
O14	12.53570	12.53570	12.86236
O15	12.57912	7.13956	12.90581
O16	7.13956	12.57912	12.90581
O17	15.24798	9.80842	10.13510
O18	9.80842	15.24798	10.13510
O19	9.85184	9.85184	10.17852
O20	12.57912	15.24798	10.13510
O21	12.53570	9.85184	10.17852
O22	7.13956	9.80842	10.13510
O23	15.24798	12.57912	10.1351
O24	9.85184	12.53570	10.17852
O25	9.80842	7.13956	10.13510
O26	12.53570	12.53570	10.17852
O27	12.57912	7.13956	10.13510
O28	7.13956	12.57912	10.13510
O29	9.80842	9.80842	7.46624
O30	9.80842	12.57912	7.46624
O31	12.57912	9.80842	7.46624
O32	12.57912	12.57912	7.46624

Table S5. Cartesian atomic coordinates (Å) of the cluster $Ce_{19}O_{32}$ (**b1**) optimised at the SP LDA+U level; the state corresponds to partially localised Ce4*f* electrons (see Table 4) and is characterised by the total energy value -435.93 eV.

Ce1	11.19377	11.19377	16.65434
Ce2	13.78561	11.19377	14.18664
Ce3	8.60193	11.19377	14.18664
Ce4	11.19377	13.85183	14.22039
Ce5	11.19377	8.53571	14.22039
Ce6	13.77719	13.81227	11.52045
Ce7	13.77719	8.57527	11.52045
Ce8	8.61035	13.81227	11.52045
Ce9	8.61035	8.57527	11.52045
Ce10	16.22809	11.19377	11.52045
Ce11	11.19377	16.26411	11.52045
Ce12	11.19377	11.19377	11.52045
Ce13	11.19377	6.12341	11.52045
Ce14	6.15942	11.19377	11.52045
Ce15	13.78561	11.19377	8.85425
Ce16	8.60193	11.19377	8.85425
Ce17	11.19377	13.85183	8.82050
Ce18	11.19377	8.53571	8.82050
Ce19	11.19377	11.19377	6.38655
O1	9.76838	9.82584	15.59680
O2	12.61916	9.82584	15.59680
O3	9.76838	12.56170	15.59680
O4	12.61916	12.56170	15.59680
O5	15.17812	9.77645	12.88979
O6	9.74197	15.22533	12.86529
O7	9.87035	9.86757	12.83978
O8	15.17812	12.61109	12.88979
O9	9.87035	12.51997	12.83978
O10	9.74197	7.16221	12.86529
O11	12.64556	15.22533	12.86529
O12	12.51719	9.86757	12.83978
O13	7.20942	9.77645	12.88979
O14	12.51719	12.51997	12.83978
O15	12.64556	7.16221	12.86529
O16	7.20942	12.61109	12.88979
O17	15.17812	9.77645	10.15112
O18	9.74197	15.22533	10.17562
O19	9.87035	9.86757	10.20111
O20	12.64556	15.22533	10.17562
O21	12.51719	9.86757	10.20111
O22	7.20942	9.77645	10.15112
O23	15.17812	12.61109	10.15112
O24	9.87035	12.51997	10.20111
O25	9.74197	7.16221	10.17562
O26	12.51719	12.51997	10.20111
O27	12.64556	7.16221	10.17562
O28	7.20942	12.61109	10.15112
O29	9.76838	9.82584	7.44411
O30	9.76838	12.56170	7.44411
O31	12.61916	9.82584	7.44411
O32	12.61916	12.56170	7.44411

Table S6. Cartesian atomic coordinates (Å) of the cluster $Ce_{19}O_{32}$ (**b1**) optimised at the SP LDA+U level; the state corresponds to fully localised Ce4*f* electrons (see Table 4) and is characterised by the total energy value -437.67 eV.

Ce1	10.81482	11.27949	16.46965
Ce2	13.65990	11.25214	14.18546
Ce3	8.27475	11.27400	13.86012
Ce4	10.98344	13.84300	14.00776
Ce5	10.95607	8.68231	14.04707
Ce6	13.79515	13.88470	11.53507
Ce7	13.72493	8.61362	11.56782
Ce8	8.52982	13.87129	11.21488
Ce9	8.46240	8.60150	11.25676
Ce10	16.21404	11.17626	11.60927
Ce11	11.11363	16.33312	11.44910
Ce12	11.12748	11.24317	11.39254
Ce13	11.13348	6.15458	11.52424
Ce14	6.05343	11.30690	10.99042
Ce15	13.86517	11.21313	8.91369
Ce16	8.71419	11.23322	8.60401
Ce17	11.30909	13.92072	8.74590
Ce18	11.26940	8.52664	8.78408
Ce19	11.43810	11.20561	6.31668
O1	9.51630	9.84614	15.34931
O2	12.22708	9.82819	15.50489
O3	9.53948	12.71589	15.32033
O4	12.24864	12.69779	15.48774
O5	15.07774	9.73203	12.92144
O6	9.62666	15.20183	12.73925
O7	9.73152	9.93722	12.66012
O8	15.18225	12.56970	12.94633
O9	9.73195	12.58425	12.61224
O10	9.71361	7.24602	12.87203
O11	12.35999	15.26421	12.97097
O12	12.36405	9.92088	12.79217
O13	6.91249	9.93498	12.46502
O14	12.36189	12.57017	12.79353
O15	12.45569	7.30361	12.96692
O16	7.02117	12.77180	12.40962
O17	15.14570	9.77317	10.18269
O18	9.72904	15.28516	10.00412
O19	9.88004	9.92834	9.99191
O20	12.56480	15.36225	10.12959
O21	12.52365	9.90214	10.17307
O22	7.20703	9.94882	9.63217
O23	15.23821	12.51314	10.09967
O24	9.89297	12.56743	9.99159
O25	9.85078	7.10673	10.02997
O26	12.53930	12.53875	10.12993
O27	12.68201	7.18139	10.23992
O28	7.28868	12.69060	9.68442
O29	9.93818	9.85527	7.29139
O30	9.94888	12.56798	7.27588
O31	12.79999	9.85483	7.47005
O32	12.81314	12.56913	7.44232

Table S7. Cartesian atomic coordinates (Å) of the cluster $Ce_{44}O_{80}$ (**c1**) optimised at the SR LDA+U level; the state corresponds to the lowest calculated single-point SP LDA+U energy for the optimal SR geometry (SP//SR), -1070.60 eV.

Ce1	13.89378	13.89378	21.96472
Ce2	16.53495	13.89378	19.58134
Ce3	11.25257	13.89378	19.58134
Ce4	13.89378	16.53495	19.58134
Ce5	13.89378	11.25257	19.58134
Ce6	16.60348	16.60348	17.06945
Ce7	16.60348	11.18405	17.06945
Ce8	11.18405	16.60348	17.06945
Ce9	11.18405	11.18405	17.06945
Ce10	19.11535	13.89378	17.00092
Ce11	13.89378	19.11535	17.00092
Ce12	13.89378	13.89378	16.98433
Ce13	13.89378	8.67218	17.00092
Ce14	8.67218	13.89378	17.00092
Ce15	21.49872	13.89378	14.35974
Ce16	16.53495	19.11535	14.35974
Ce17	16.51836	13.89378	14.35974
Ce18	16.53495	8.67218	14.35974
Ce19	11.25257	19.11535	14.35974
Ce20	11.26917	13.89378	14.35974
Ce21	11.25257	8.67218	14.35974
Ce22	6.28881	13.89378	14.35974
Ce32	19.11535	16.53495	14.35974
Ce24	19.11535	11.25257	14.35974
Ce25	13.89378	21.49872	14.35974
Ce26	3.89378	16.51836	14.35974
Ce27	13.89378	11.26917	14.35974
Ce28	13.89378	6.28881	14.35974
Ce29	8.67218	16.53495	14.35974
Ce30	8.67218	11.25257	14.35974
Ce31	16.60348	16.60348	11.65004
Ce32	16.60348	11.18405	11.65004
Ce33	11.18405	16.60348	11.65004
Ce34	11.18405	11.18405	11.65004
Ce35	19.11535	13.89378	11.71857
Ce36	13.89378	19.11535	11.71857
Ce37	13.89378	13.89378	11.73516
Ce38	13.89378	8.67218	11.71857
Ce39	8.67218	13.89378	11.71857
Ce40	16.53495	13.89378	9.13815
Ce41	11.25257	13.89378	9.13815
Ce42	13.89378	16.53495	9.13815
Ce43	13.89378	11.25257	9.13815
Ce44	13.89378	13.89378	6.75477
O1	12.51816	12.51816	21.02804
O2	15.26937	12.51816	21.02804
O3	12.51816	15.26937	21.02804
O4	15.26937	15.26937	21.02804
O5	17.93468	12.50619	18.40064
O6	12.50619	17.93468	18.40064
O7	12.55677	12.55677	18.34983

O8	17.93468	15.28134	18.40064
O9	12.55677	15.23076	18.34983
O10	12.50619	9.85285	18.40064
O11	15.28134	17.93468	18.40064
O12	15.23076	12.55677	18.34983
O13	9.85285	12.50619	18.40064
O14	15.23076	15.23076	18.34983
O15	15.28134	9.85285	18.40064
O16	9.85285	15.28134	18.40064
O17	17.93468	17.93468	15.74733
O18	17.88386	12.55677	15.69673
O19	12.55677	17.88386	15.69673
O20	12.53680	12.53680	15.71670
O21	12.51816	7.22545	15.73534
O22	7.22545	12.51816	15.73534
O23	20.56208	12.51816	15.73534
O24	15.23076	17.88386	15.69673
O25	15.25073	12.53680	15.71670
O26	15.26937	7.22545	15.73534
O27	9.85285	17.93468	15.74733
O28	9.90367	12.55677	15.69673
O29	7.88386	15.23076	15.69673
O30	17.93468	9.85285	15.74733
O31	12.51816	20.56208	15.73534
O32	12.53680	15.25073	15.71670
O33	12.55677	9.90367	15.69673
O34	7.22545	15.26937	15.73534
O35	20.56208	15.26937	15.73534
O36	15.26937	20.56208	15.73534
O37	15.25073	15.25073	15.71670
O38	15.23076	9.90367	15.69673
O39	9.90367	15.23076	15.69673
O40	9.85285	9.85285	15.74733
O41	17.93468	17.93468	12.97216
O42	17.88386	12.55677	13.02276
O43	12.55677	17.88386	13.02276
O44	12.53680	12.53680	13.00279
O45	12.51816	7.22545	12.98412
O46	7.22545	12.51816	12.98412
O47	17.88386	15.23076	13.02276
O48	17.93468	9.85285	12.97216
O49	12.51816	20.56208	12.98412
O50	12.53680	15.25073	13.00279
O51	12.55677	9.90367	13.02276
O52	7.22545	15.26937	12.98412
O53	20.56208	12.51816	12.98412
O54	15.23076	17.88386	13.02276
O55	15.25073	12.53680	13.00279
O56	15.26937	7.22545	12.98412
O57	9.85285	17.93468	12.97216
O58	9.90367	12.55677	13.02276
O59	20.56208	15.26937	12.98412
O60	15.26937	20.56208	12.98412
O61	15.25073	15.25073	13.00279
O62	15.23076	9.90367	13.02276

O63	9.90367	15.23076	13.02276
O64	9.85285	9.85285	12.97216
O65	17.93468	12.50619	10.31884
O66	12.50619	17.93468	10.31884
O67	12.55677	12.55677	10.36966
O68	15.28134	17.93468	10.31884
O69	15.23076	12.55677	10.36966
O70	9.85285	12.50619	10.31884
O71	17.93468	15.28134	10.31884
O72	12.55677	15.23076	10.36966
O73	12.50619	9.85285	10.31884
O74	15.23076	15.23076	10.36966
O75	15.28134	9.85285	10.31884
O76	9.85285	15.28134	10.31884
O77	12.51816	12.51816	7.69142
O78	12.51816	15.26937	7.69142
O79	15.26937	12.51816	7.69142
O80	15.26937	15.26937	7.69142

Table S8. Cartesian atomic coordinates (Å) of the cluster $Ce_{44}O_{80}$ (**c1**) optimised at the SP LDA+U level; the state corresponds to the lowest calculated energy -1072.46 eV.

Ce1	13.89378	13.89378	21.96549
Ce2	16.56947	13.89378	19.59850
Ce3	11.21806	13.89378	19.59850
Ce4	13.89378	16.56947	19.59850
Ce5	13.89378	11.21806	19.59850
Ce6	16.60848	16.60848	17.07445
Ce7	16.60848	11.17905	17.07445
Ce8	11.17905	16.60848	17.07445
Ce9	11.17905	11.17905	17.07445
Ce10	19.13251	13.89378	17.03544
Ce11	13.89378	19.13251	17.03544
Ce12	13.89378	13.89378	17.00200
Ce13	13.89378	8.65502	17.03544
Ce14	8.65502	13.89378	17.03544
Ce15	21.49950	13.89378	14.35974
Ce16	16.56947	19.13251	14.35974
Ce17	16.53603	13.89378	14.35974
Ce18	16.56947	8.65502	14.35974
Ce19	11.21806	19.13251	14.35974
Ce20	11.25149	13.89378	14.35974
Ce21	11.21806	8.65502	14.35974
Ce22	6.28803	13.89378	14.35974
Ce23	19.13251	16.56947	14.35974
Ce24	19.13251	11.21806	14.35974
Ce25	13.89378	21.49950	14.35974
Ce26	13.89378	16.53603	14.35974
Ce27	13.89378	11.25149	14.35974
Ce28	13.89378	6.28803	14.35974
Ce29	8.65502	16.56947	14.35974
Ce30	8.65502	11.21806	14.35974
Ce31	16.60848	16.60848	11.64504

Ce32	16.60848	11.17905	11.64504
Ce33	11.17905	16.60848	11.64504
Ce34	11.17905	11.17905	11.64504
Ce35	19.13251	13.89378	11.68405
Ce36	13.89378	19.13251	11.68405
Ce37	13.89378	13.89378	11.71749
Ce38	13.89378	8.65502	11.68405
Ce39	8.65502	13.89378	11.68405
Ce40	16.56947	13.89378	9.12098
Ce41	11.21806	13.89378	9.12098
Ce42	13.89378	16.56947	9.12098
Ce43	13.89378	11.21806	9.12098
Ce44	13.89378	13.89378	6.75400
O1	12.53737	12.53737	21.08901
O2	15.25016	12.53737	21.08901
O3	12.53737	15.25016	21.08901
O4	15.25016	15.25016	21.08901
O5	17.93472	12.45711	18.40069
O6	12.45711	17.93472	18.40069
O7	12.56204	12.56204	18.34947
O8	17.93472	15.33042	18.40069
O9	12.56204	15.22549	18.34947
O10	12.45711	9.85281	18.40069
O11	15.33042	17.93472	18.40069
O12	15.22549	12.56204	18.34947
O13	9.85281	12.45711	18.40069
O14	15.22549	15.22549	18.34947
O15	15.33042	9.85281	18.40069
O16	9.85281	15.33042	18.40069
O17	17.93472	17.93472	15.79641
O18	17.88351	12.56204	15.69146
O19	12.56204	17.88351	15.69146
O20	12.54364	12.54364	15.70986
O21	12.53737	7.16449	15.71612
O22	7.16449	12.53737	15.71612
O23	20.62304	12.53737	15.71612
O24	15.22549	17.88351	15.69146
O25	15.24389	12.54364	15.70986
O26	15.25016	7.16449	15.71612
O27	9.85281	17.93472	15.79641
O28	9.90402	12.56204	15.69146
O29	17.88351	15.22549	15.69146
O30	17.93472	9.85281	15.79641
O31	12.53737	20.62304	15.71612
O32	12.54364	15.24389	15.70986
O33	12.56204	9.90402	15.69146
O34	7.16449	15.25016	15.71612
O35	15.25016	20.62304	15.71612
O37	15.24389	15.24389	15.70986
O38	15.22549	9.90402	15.69146
O39	9.90402	15.22549	15.69146
O40	9.85281	9.85281	15.79641
O41	17.93472	17.93472	12.92308
O42	17.88351	12.56204	13.02803
O43	12.56204	17.88351	13.02803

O44	12.54364	12.54364	13.00963
O45	12.53737	7.16449	13.00334
O46	7.16449	12.53737	13.00334
O47	17.88351	15.22549	13.02803
O48	17.93472	9.85281	12.92308
O49	12.53737	20.62304	13.00334
O50	12.54364	15.24389	13.00963
O51	12.56204	9.90402	13.02803
O52	7.16449	15.25016	13.00334
O53	20.62304	12.53737	13.00334
O54	15.22549	17.88351	13.02803
O55	15.24389	12.54364	13.00963
O56	15.25016	7.16449	13.00334
O57	9.85281	17.93472	12.92308
O58	9.90402	12.56204	13.02803
O59	20.62304	15.25016	13.00334
O60	15.25016	20.62304	13.00334
O61	15.24389	15.24389	13.00963
O62	15.22549	9.90402	13.02803
O63	9.90402	15.22549	13.02803
O64	9.85281	9.85281	12.92308
O65	17.93472	12.45711	10.31880
O66	12.45711	17.93472	10.31880
O67	12.56204	12.56204	10.37002
O68	15.33042	17.93472	10.31880
O69	15.22549	12.56204	10.37002
O70	9.85281	12.45711	10.31880
O71	17.93472	15.33042	10.31880
O72	12.56204	15.22549	10.37002
O73	12.45711	9.85281	10.31880
O74	15.33042	9.85281	10.31880
O76	9.85281	15.33042	10.31880
O77	12.53737	12.53737	7.63045
O78	12.53737	15.25016	7.63045
O79	15.25016	12.53737	7.63045
O80	15.25016	15.25016	7.63045