Electronic Supplementary Material (ESI) for Dalton Transactions.
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Experimental Section

Materials. ADPTZ solutions in methanol were prepared as described previously.[1] The plutonium stock solution was prepared as follow. After dissolution of 55 mg of pure Cs_2PuCl_6 compound (0.0018 mol % Pu-238, 97.090 mol % Pu-239, 2.869 mol % Pu-240, 0.00299 mol % Pu-241, 0.0084 mol % Pu-242) in 0.2 M NH_3OH^+, Cl^- to reduce Pu(IV) to Pu(III), Pu(III) hydroxide was precipitated with concentrated ammoniac then washed with 0.1M NH_3 + 0.001M NH_3OH^+, Cl^- and quickly dissolved in HCl, NH_3OH^+, Cl^- to avoid oxidation and hydrolysis. Few microliters of tetramethylammonium hydroxide were added gently to the solution to raise the pH to 3.5. The Pu(III) oxidation state was checked by UV-vis spectrophotometry and the Pu stock solution was titrated by spectrophotometry after oxidation with Ce(IV) of an aliquot of the Pu(III) solution to Pu(VI).

The curium stock solution was prepared by dissolution of 1 mg of $^{244}CmO_2$ in 4 M HNO_3, and purified using a Dowex anion exchange resin after increasing the acidity to 7 M HNO_3 in order to sorb $^{240}Pu(IV)$ (α decay of ^{244}Cm) on the resin and separate it from Cm(III). After five cycles of resin purification, the remaining amount of ^{240}Pu was separated from Cm by solvent extraction with 30% TBP diluted in hydrogenated tetrapropylene (TPH). After Cm/Pu separation, curium hydroxide was then precipitated by adding sodium hydroxide, washed and redissolved in dilute HCl. The pH of the Cm^{3+} solution was then adjusted to 3.6 with few drops of 0.1 M tetramethylammonium hydroxide and the curium concentration in this stock solution (0.00021 M) was measured by α-spectrometry.

The samples were prepared by addition of weighed amounts of the ADPTZ and actinide stock solutions and of sufficient water and methanol (MeOH) to maintain a constant 71/29 mass % MeOH/H_2O ratio and to take into account the volumic contraction between water and methanol. It is then possible to transpose to the volumic proportions (corresponding to 75/25 vol %) knowing the density of the different solutions. The pH of the mixed solution was about 5 for each sample. The pKas of ADPTZ, determined by UV-spectrophotometry in 75/25 vol % methanol/water, are $pKa_1 = 1.7$ and $pKa_2 = 3.5$,[1] which assure nearly complete deprotonation of the ADPTZ ligand in the samples at pH = 5. Background electrolytes were not added to the solutions to control the ionic strength of the solutions because trial runs indicated that interactions between polyaromatic ligands and common alkali metal cations would skew the measured thermodynamic parameters. However, given the low concentrations of the neutral ligand and of the metal ions (10^{-5} to 10^{-2} M), the ratio of the solute activity coefficients was considered constant.

Spectrophotometric titrations. Titrations of ADPTZ by Pu(III) and Cm(III) were carried out with a Shimadzu 3101 spectrophotometer in a glove-box. Actinide complexation was studied by following the ligand π-π^* absorption bands (200-400 nm) with increasing concentrations of the actinide ion. Generally, seven samples with a constant concentration of ADPTZ were used with [An(III)]/[ADPTZ] ratios between 0 and 6. Spectra were measured at different temperatures (every 5°C from 10 to 55 °C) to determine the enthalpy and entropy of complexation using the van't Hoff relation (1), where β is the stability constant for complex formation:

$$\ln \beta = -\frac{\Delta H^0}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^0}{R} \qquad (1)$$

For Pu(III), the stability constants determined at temperatures above 30°C were not considered because of the presence of Pu(IV) due to Pu(III) oxidation at high temperature.

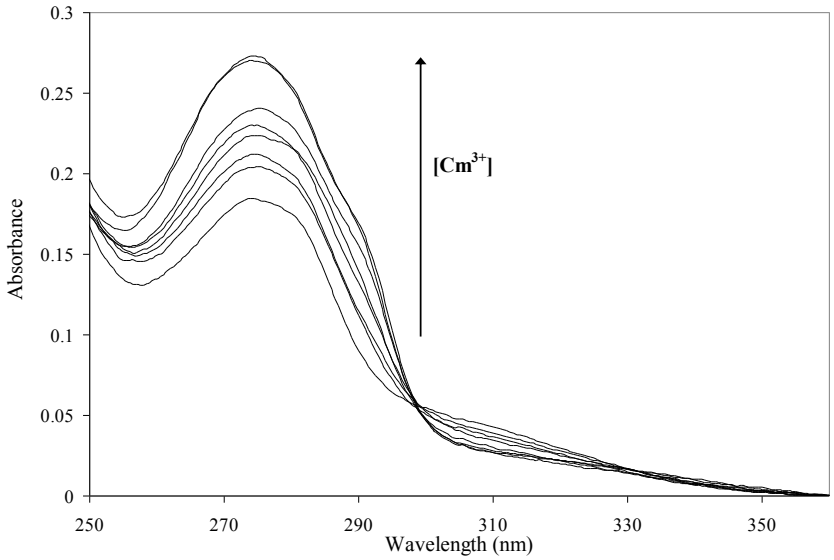

Figure 1. Spectrophotometric titration of a Cm-ADPTZ solution with increasing concentrations of Cm^{3+} in 75/25 vol % MeOH/H_2O at 25°C, path length: 1 cm, 0 < [Cm]/[ADPTZ] < 6.

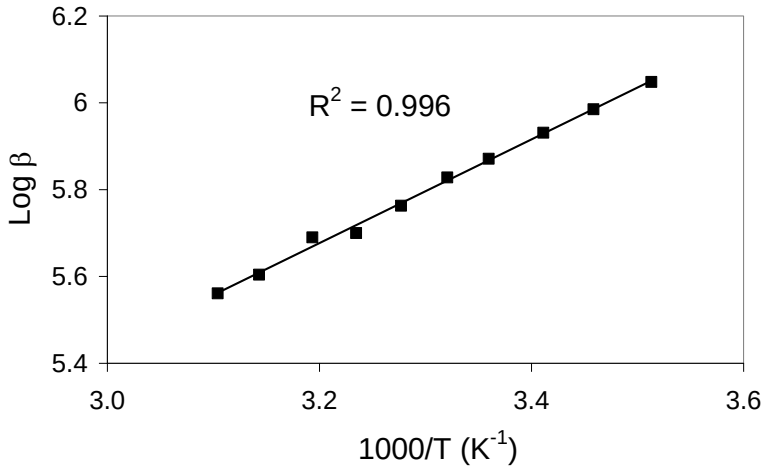

Figure 2. Temperature dependence of the stability constants for Cm^{3+} complexation by ADPTZ

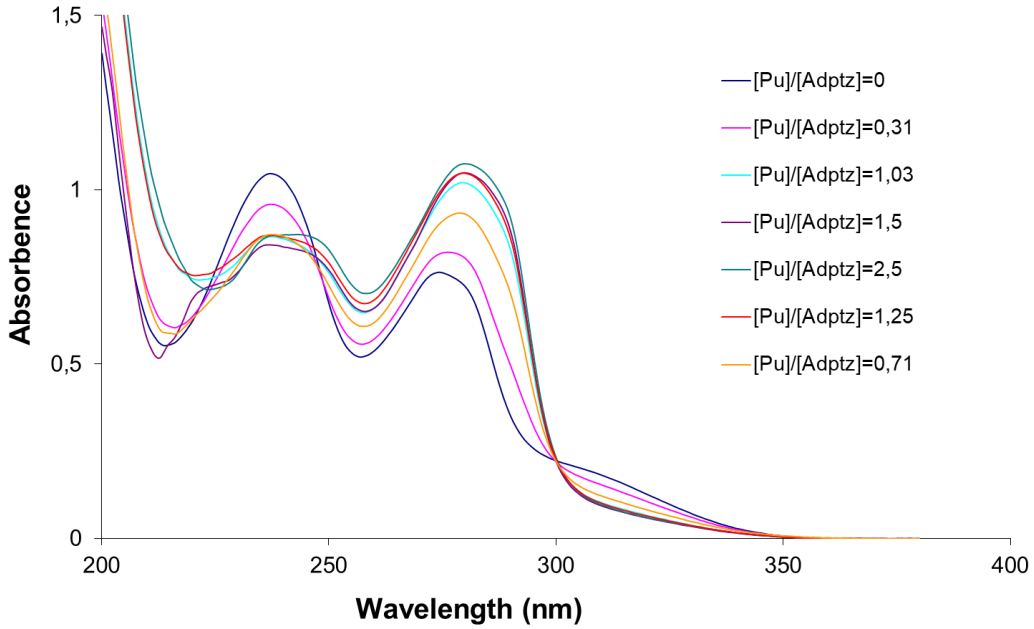

Figure 3. Spectrophotometric titration of a Pu-ADPTZ solution with increasing concentrations of Pu^{3+} in 75/25 vol % MeOH/H_2O at 25°C.

Table 1. Stability constants (log β_1) for 1:1 plutonium(III) and curium(III) complexes with ADPTZ in 75/25 vol % methanol/water at different temperatures between 5 and 55°C.

	log β_1									
T (°C)	10	15	20	25	30	35	40	45	50	55
Pu^{3+}	6.04	5.92	5.85	5.73	5.60	-	5.37	-	5.12	-
Cm^{3+}	6.05	5.99	5.93	5.87	5.83	5.76	5.70	5.69	5.60	5.56

Microcalorimetric studies. Microcalorimetric titrations were performed using a Thermal Activity Monitor microcalorimeter (Thermometric) in a glove-box. Titration conditions were optimized with "cold" experiments on Eu^{3+}-ADPTZ system to fit the experimental parameters to the Pu(III) solution. After confirming the formation enthalpy of the $EuADPTZ^{3+}$ system determined previously[1], the same experimental conditions were applied to plutonium(III). Three titrations were carried out at 25.000 ± 0.0005°C beginning with 2.8 mL of 3×10^{-4} M Pu^{3+} in 75/25 vol % MeOH/H_2O in the glass reaction cell. The heats of formation of the 1:1 $PuADPTZ^{3+}$ complexes were measured by adding 15 µL aliquots of 5.6×10^{-3} M ADPTZ in 75/25 vol % MeOH/H_2O to the reaction cell. The necessary corrections for the heats of dilution of the metal ions were determined in separate blank runs for each of the three titrations. Pu(III) being quite unstable in aqueous solution, oxidation state was checked by UV-vis spectrophotometry at the end of each titration to confirm the absence of oxidation. The stability constants of the Pu(III)-ADPTZ complexes were either obtained from the spectrophotometry or by simultaneously fitting the stability constant and the enthalpy of complexation to the calorimetric data.

Microcalorimetric data were analyzed by the following method. After each addition *i* of titrant, an observed heat Q^i is released. The observed heat released after each addition corresponds to the sum of

the heat of formation of the $PuADPTZ^{3+}$ complex $Q^{i}_{complex}$ and the heat of dilution Q^{i}_{dil}. For *k* additions, the cumulative reaction heat Q^{k}_{total} is defined as:

$$Q^{k}_{total} = \sum_{i=1}^{k} Q^{i} \quad (2)$$

A positive sign is associated with an exothermic heat. The complexation enthalpy for the formation of the 1:1 $PuADPTZ^{3+}$ complex, ΔH^0, is directly correlated to the dilution corrected heat by the following relation:

$$Q^{i}_{complex} = Q^{i} - Q^{i}_{dil} = -\Delta H^{0}.\,\Delta n^{i}_{PuADPTZ} \quad (3)$$

where $\Delta n^{i}_{PuAdptz}$ is the number of moles of complex formed after the i^{th} addition, which can be calculated at each point of the titration from the stability constant measured by spectrophotometry ($\log \beta_1 = 5.70$), considering the formation of the only 1:1 complex. The reaction heats corrected by the heat of dilution for the plutonium(III) titration experiments are plotted in Figure 2 versus the number of moles of complex formed for each of the three experiments. The linear trends observed for the first ten additions of ligand confirm the formation of the 1:1 complex and the possibility to calculate the complexation enthalpy from the slope of the linear regression. However, at the end of the titration, the trend is no linear anymore which means that another heat must be taken into account. That heat release could be attributed to the formation of a second complex for high [ADTPZ]/[Pu] ratios or to a parasite heat as association or specific dilution in case of concentrated ADPTZ solutions. The complexation enthalpy of Pu(III) was therefore estimated from the slope of the linear part of each titration and $\Delta H^{0}_{(PuADPTZ)}$ was obtained from the average of the three experiments.

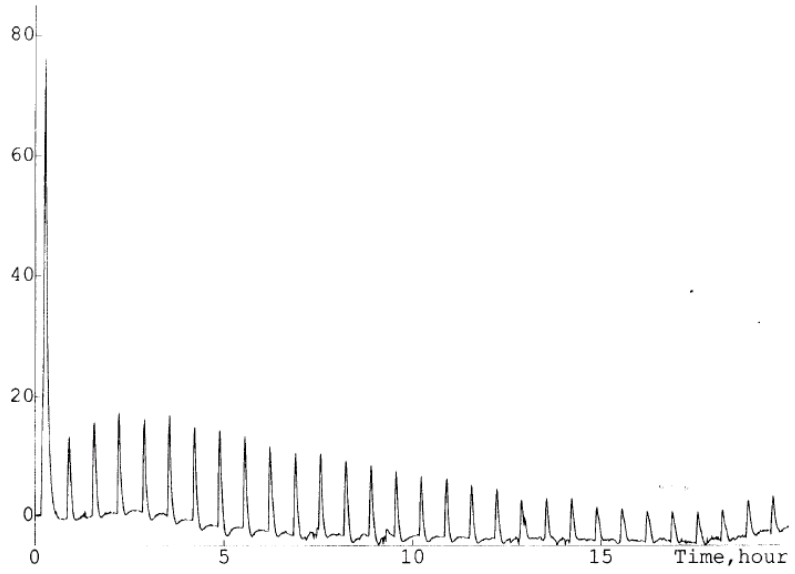

Figure 4. Microcalorimetric titration of 2.8 mL of 3×10^{-4} M Pu^{3+} by addition of 5.6×10^{-3} M ADPTZ in 75/25 vol % $MeOH/H_2O$ at 25°C**.**

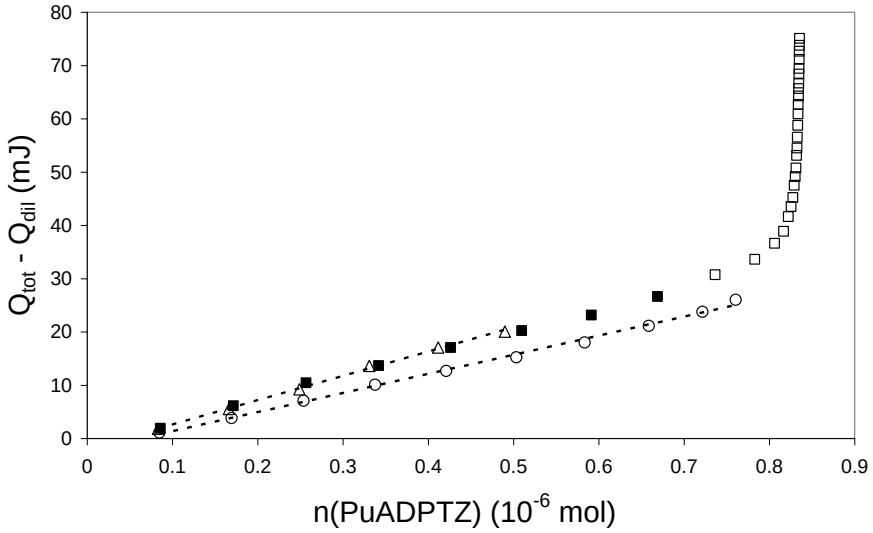

Figure 5. Corrected heat measured (Q_{total}- Q_{dil}) for the three microcalorimetric titrations of a 3×10^{-4} M Pu^{3+} by ADPTZ in 75/25 vol % MeOH/H_2O at 25°C**.**

DFT calculations. The geometries of the $M(H_2O)_9^{3+}$ and $ML(H_2O)_6^{3+}$ complexes were optimized at the DFT level of theory with the Gaussian 09 program package. The optimized structures were characterized as true minima through harmonic vibrational frequency analysis in the gaz phase. Calculations in methanol solution were performed using the Integral Equation Formalism Polarizable Continuum Model (IEFPCM).

For the metal ions, small-core relativistic effective core potentials (RECP) developed in the Stuttgart/Cologne group were used together with the accompanying basis set to describe the valence electron density.[2, 3] For other atoms, the 6-31+G(d,p)* basis set was used. The B3LYP functional was employed.

Table 2. Thermodynamic parameters for the exchange reaction $M_1(H_2O)_9^{3+} + M_2L(H_2O)_6^{3+} \rightarrow M_2(H_2O)_9^{3+} + M_1L(H_2O)_6^{3+}$ (CN=9) and $M_1(H_2O)_8^{3+} + M_2L(H_2O)_5^{3+} \rightarrow M_2(H_2O)_8^{3+} + M_1L(H_2O)_5^{3+}$ (CN=8) ($\Delta\Delta H^0$ and $T\Delta\Delta S^0$ in kJ mol^{-1} at T=298 K) calculated at the DFT/B3LYP level in the gas phase.

	CN=9		CN=8	
	$\Delta\Delta H^0$	$T\Delta\Delta S^0$	$\Delta\Delta H^0$	$T\Delta\Delta S^0$
Pu/Am	+2	-2	+1	1
Am/Cm	+6	0	+5	0
Pr/Pu	-17	-1	-16	-3
Nd/Am	-9	+1	-8	1
Nd/Cm	-3	-1	-3	+1

Table 3. Thermodynamic parameters ($\Delta\Delta G^0$ in kJ mol^{-1} at T=298 K) for the exchange reaction $M_1(H_2O)_9^{3+} + M_2L(H_2O)_6^{3+} \rightarrow M_2(H_2O)_6^{3+} + M_1L(H_2O)_6^{3+}$ (CN=9) calculated at the DFT/B3LYP level in in solution (IEFPCM model, methanol).

	$\Delta\Delta G^0$ gaz	$\Delta\Delta G^0$ sol
Pu/Am	4	+3

Am/Cm	+6	+7
Pr/Pu	-16	-17
Nd/Am	-10	-7
Nd/Cm	-2	-4

1. M. Miguirditchian, D. Guillaneux, D. Guillaumont, P. Moisy, C. Madic, M. P. Jensen and K. L. Nash, *Inorg. Chem.*, 2005, **44**, 1404-1412.
2. X. Y. Cao and M. Dolg, *J. Mol. Struc. THEOCHEM*, 2004, **673**, 203-209.
3. X. Y. Cao, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2003, **118**, 487-496.

Cartesian coordinates of PuAdptz$(H_2O)_6^{3+}$ optimized in the gas phase.

Pu	0.00000000	0.00000000	0.00000000
N	0.00000000	0.00000000	2.49474400
N	2.33997248	0.00000000	1.13236768
N	-2.33979316	-0.00105237	1.13218219
C	1.14660342	-0.03098412	3.23635936
N	1.19764880	-0.03578119	4.54842502
C	-0.00008796	0.00153840	5.19578307
N	-1.19778834	0.03833160	4.54830442
C	-1.14663885	0.03197268	3.23626046
N	-0.00013525	0.00216530	6.51962092
C	3.49166101	0.03958901	0.42826440
C	4.75344324	0.02017729	1.02297622
C	4.83682836	-0.04382327	2.41502920
C	3.65452365	-0.06975721	3.15858234
C	2.43014480	-0.04177292	2.48803106
C	-2.43012296	0.04209692	2.48779397
C	-3.65458633	0.07063310	3.15815687
C	-4.83679684	0.04376541	2.41448711
C	-4.75321357	-0.02185385	1.02251335
C	-3.49136444	-0.04174103	0.42795365
O	-0.73401135	-2.43380411	0.42772044
O	0.73279365	2.43425901	0.43241407
O	1.49469993	-1.88057583	-1.13879053
O	1.18421678	1.11789656	-2.09224236
O	-1.49453830	1.88116630	-1.13728875
O	-1.18270193	-1.11325592	-2.09561269
H	0.87265166	-0.02576550	7.03277388
H	-0.87295785	0.03057381	7.03268894
H	3.66469221	-0.10698139	4.24152907
H	5.80117879	-0.06600902	2.91352898
H	5.64445977	0.05617518	0.40455561
H	3.39591103	0.09810570	-0.65204516
H	-3.66484659	0.10892290	4.24106857
H	-5.80122115	0.06636822	2.91282739
H	-5.64413852	-0.05880012	0.40401496
H	-3.39562580	-0.10177279	-0.65228987
H	-1.43001839	-2.73946526	1.02918021
H	-0.12567211	-3.17804148	0.29874976
H	-1.58275530	-1.99266119	-2.00625473
H	-1.50028940	-0.75582394	-2.93919826
H	-2.38308497	2.19037399	-0.90247549
H	-1.28835331	2.27382108	-1.99971069
H	1.29189472	-2.27042176	-2.00329126
H	2.38253224	-2.19030062	-0.90194074
H	1.58516051	1.99659416	-2.00001367
H	1.50040877	0.76332016	-2.93755889
H	1.42978036	2.73973373	1.03284128
H	0.12319800	3.17800748	0.30658640

Cartesian coordinates of AmAdptz$(H_2O)_6^{3+}$ optimized in the gas phase.

Am	0.03211700	-1.04195400	0.00768300
N	-0.03266200	1.43915900	0.00271000
N	-2.34820700	0.02647800	-0.02312900
N	2.32897900	0.12454700	-0.03772600
C	-1.19535800	2.15452000	-0.03718600
N	-1.27269800	3.46569200	-0.04210800
C	-0.08968300	4.13854400	0.00359700
N	1.12194100	3.51681400	0.03611600
C	1.09796000	2.20415600	0.02934900
N	-0.11814800	5.46208900	0.01394400
C	-3.48778200	-0.69655500	0.00266200
C	-4.76010500	-0.12502600	-0.03045800
C	-4.86828600	1.26512000	-0.09189400
C	-3.69912500	2.02941900	-0.10137900
C	-2.46334900	1.38032600	-0.06211600
C	2.39513300	1.48086000	0.02478300
C	3.60749600	2.17246600	0.05406900
C	4.80243300	1.45043900	0.00839900
C	4.74313900	0.05822000	-0.07680500
C	3.49221600	-0.55873500	-0.09722200
O	0.65037400	-0.58031300	-2.45220200
O	-0.62725900	-0.47551100	2.45708400
O	-1.42598000	-2.33607200	-1.80579600
O	-1.17941800	-3.01158300	1.25075600
O	1.53368000	-2.15246300	1.85513200
O	1.26471900	-3.09904900	-1.09123600
H	-1.00172600	5.95649000	-0.01333100
H	0.74335300	5.99373900	0.04600000
H	-3.72836600	3.11209500	-0.13481100
H	-5.84107000	1.74634400	-0.12414200
H	-5.63997600	-0.75977700	-0.00646400
H	-3.37410600	-1.77462600	0.06364800
H	3.59841200	3.25483600	0.10687600
H	5.75804800	1.96550300	0.03097100
H	5.64462800	-0.54360500	-0.12968400
H	3.41467200	-1.63909000	-0.17462600
H	1.30056300	0.05205900	-2.79432700
H	0.04005400	-0.77487200	-3.18025300
H	1.63911600	-3.02610500	-1.98340700
H	1.62454100	-3.91564400	-0.71166500
H	2.43882200	-1.94626400	2.13480200
H	1.28424200	-2.97233800	2.30915300
H	-1.16869700	-3.19667500	-2.17113200
H	-2.32307800	-2.15976000	-2.12856800
H	-1.56290400	-2.84387100	2.12629200
H	-1.52963800	-3.86631900	0.95568900
H	-1.30366900	0.15532800	2.74728600
H	0.00417200	-0.55791200	3.18841300

Cartesian coordinates of CmAdptz$(H_2O)_6^{3+}$ optimized in the gas phase.

Cm	0.00000000	0.00000000	1.04321600
N	0.00000000	0.00000000	-1.43905900
N	0.00335100	2.34287000	-0.07072500
N	-0.00335100	-2.34287000	-0.07072500
C	-0.03944900	1.14644800	-2.17746000
N	-0.04558600	1.19783200	-3.49001500
C	0.00000000	0.00000000	-4.13707000
N	0.04558600	-1.19783200	-3.49001500
C	0.03944900	-1.14644800	-2.17746000
N	0.00000000	0.00000000	-5.46116400
C	0.04040400	3.49774400	0.62759800
C	0.00000000	4.75772000	0.03043100
C	-0.08066400	4.83694900	-1.36070600
C	-0.10240200	3.65208000	-2.10005100
C	-0.05562400	2.42968500	-1.42680700
C	0.05562400	-2.42968500	-1.42680700
C	0.10240200	-3.65208000	-2.10005100
C	0.08066400	-4.83694900	-1.36070600
C	0.00000000	-4.75772000	0.03043100
C	-0.04040400	-3.49774400	0.62759800
O	-2.45266500	-0.55940900	0.47348100
O	2.45266500	0.55940900	0.47348100
O	-1.78406400	1.45725100	2.30920100
O	1.22087800	1.26327000	2.98525500
O	1.78406400	-1.45725100	2.30920100
O	-1.22087800	-1.26327000	2.98525500
H	-0.03434300	0.87256500	-5.97425000
H	0.03434300	-0.87256500	-5.97425000
H	-0.15038500	3.65870400	-3.18257600
H	-0.11791900	5.79952200	-1.86172800
H	0.03435400	5.65055500	0.64630800
H	0.11809300	3.40681800	1.70667800
H	0.15038500	-3.65870400	-3.18257600
H	0.11791900	-5.79952200	-1.86172800
H	-0.03435400	-5.65055500	0.64630800
H	-0.11809300	-3.40681800	1.70667800
H	-2.76733500	-1.18535300	-0.19657100
H	-3.17750000	0.06551900	0.62970400
H	-2.10301100	-1.64052100	2.83981400
H	-0.89319800	-1.64174400	3.81573500
H	2.08241400	-2.36737300	2.15854100
H	2.20663500	-1.15917500	3.12964300
H	-2.20663500	1.15917500	3.12964300
H	-2.08241400	2.36737300	2.15854100
H	2.10301100	1.64052100	2.83981400
H	0.89319800	1.64174400	3.81573500
H	2.76733500	1.18535300	-0.19657100
H	3.17750000	-0.06551900	0.62970400