Supporting information

Spectroscopic speciation of aqueous Am(III)-oxalate complexes

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1. Experimental supporting information

Table S1. List of samples examined in this study with various Am(III) and Ox concentrations

Sample numbers	A (μM)		B (μM)		C (μM)		D (μM)	
	$[Am]_{total}$	$[Ox]_{total}$	$[Am]_{total}$	$[Ox]_{total}$	$[Am]_{total}$	$[Ox]_{total}$	$[Am]_{total}$	$[Ox]_{total}$
1	1.16	0	1.19	0	2.77	0	8.35	0
2	1.16	2	1.19	2	2.77	3	8.31	11
3	1.16	10	1.19	10	2.77	10	8.31	22*
4	1.16	30	1.19	25	2.76	30*	8.30	33*
5	1.16	100	1.18	50	2.76	50*	8.28	55*
6	1.15	500	1.18	99	2.76	500*	8.23	110*
7	1.15	990	1.19	200	2.74	990*	7.49	1000*
8	0.97	17000	1.18	500	2.49	10000	7.49	10000
9			1.18	990	1.94	30000	4.16	50000
10			1.16	2400				
11			1.13	5200				
12			1.07	10000				
13			1.02	14000				
14			0.83	30000				

*The samples showing a decrease in the absorbance over a week were excluded in the further analysis.

Table S2. Summary of reaction constants of hydroxo-Am(III) and oxalic acid (NEA-TDB) [1,2]

Reactions	$\log {}^*\beta^0$	$\log {}^*\beta$ (I = 0.1 M NaClO$_4$)
$Am^{3+} + H_2O \rightarrow Am(OH)^{2+} + H^+$	-7.2 ± 0.5	-7.6 ± 0.5
$Am^{3+} + 2H_2O \rightarrow Am(OH)_2^+ + 2H^+$	-15.7 ± 0.7	-15.8 ± 0.7
$Am^{3+} + 3H_2O \rightarrow Am(OH)_3 + 3H^+$	-26.2 ± 0.5	-26.9 ± 0.5
	$\log {}^*K_{s,0}{}^0$	$\log {}^*K_{s,0}$ (I = 0.1 M NaClO$_4$)
$Am(OH)_3(s, am) + 3H^+ \rightarrow Am^{3+} + 3H_2O(l)$	16.9 ± 0.8	17.6 ± 0.8
	$\log K^0$	$\log K$ (I = 0.1 M NaClO$_4$)
$Ox^{2-} + H^+ \rightarrow HOx^-$	4.25 ± 0.01	3.83 ± 0.01
$HOx^- + H^+ \rightarrow H_2Ox$	1.40 ± 0.03	1.19 ± 0.03

Table S3. Binary ion interaction coefficients (ε) and activity coefficients (a) (NEA-TDB) [1,2]

$\varepsilon(H^+, ClO_4^-)$	0.14 ± 0.02
$\varepsilon(Am^{3+}, ClO_4^-)$	0.49 ± 0.03
$\varepsilon(Am(OH)^{2+}, ClO_4^-)$	0.39 ± 0.04
$\varepsilon(Am(OH)_2^+, ClO_4^-)$	0.17 ± 0.04
$\varepsilon(Am(Ox)^+, ClO_4^-)$	0.08 ± 0.05
$\varepsilon(Na^+, Am(Ox)_2^-)$	-0.21 ± 0.08
$\varepsilon(Na^+, Ox^{2-})$	-0.08 ± 0.01
$\varepsilon(Na^+, Am(CO_3)_3^{3-})^*$	-0.23 ± 0.1
$\varepsilon(Na^+, OH^-)$	0.04 ± 0.01
$\varepsilon(Na^+, HOx^-)$	-0.07 ± 0.01
$\varepsilon(Na^+, Ox^{2-})$	-0.08 ± 0.01
$\log(a_{H2O})$	-0.001479

$^*\varepsilon(Na^+, Am(CO)_3^{3-})$ was used for the unknown $\varepsilon(Na^+, Am(Ox)_3^{3-})$.

Table S4. Deconvoluted results of Am(III) absorption spectra in the presence of 0–1 mM Na$_2$Ox, under which contribution of Na$_2$Ox to the total ionic strength is negligible and I = 0.1 M NaClO$_4$ can be applied.

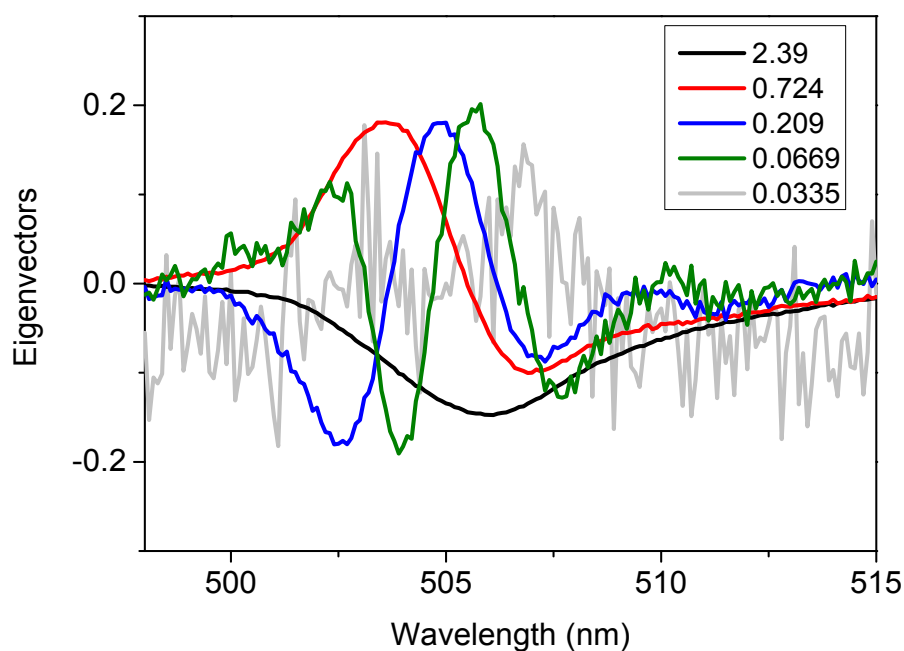| Reactions	Abs. peak	Molar abs. coeff. (M^{-1}cm^{-1})	$\log \beta_{1,n}$
$Am^{3+} + Ox^{2-} \rightarrow AmOx^+$	504.3 nm	507 ± 9	5.36 ± 0.04
$Am^{3+} + 2Ox^{2-} \rightarrow Am(Ox)_2^-$	505.7 nm	555 ± 14	9.12 ± 0.07

Figure S1. Eigenvector plots as a function of wavelength for the first five non-zero singular eigenvalues from factor analysis of the absorption spectra. The 5th curve (light gray) shows a much higher noise level compared to the first four curves, indicating that it is from errors rather than an absorbing species.[3] On the other hand, the 4th curve shows a low level of noise, although the singular eigenvalue is small. Therefore we analyzed the data with a four species model in the system.
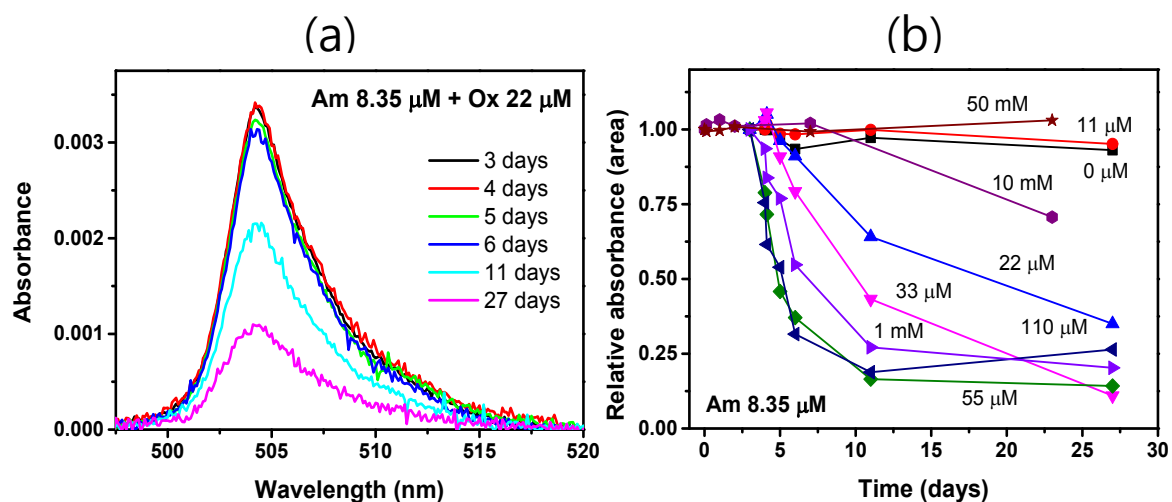

Figure S2. Time-dependent absorption spectral changes of Am(III)-Ox species. (a) Representative absorbance decrease against time. The sample contained 8.35 μM Am(III) and 22 μM Ox (b) Time-dependent absorbance change of 8.35 μM Am(III) in the presence of various concentrations of Ox. All the samples were prepared in 0.1 M NaClO$_4$ and pH ~ 6.1.

2. Computational supporting information

Evaluation of the implemented methods in the DFT calculations In order to assess the efficacy of the level of theory implemented herein, the geometry of $AmCl_6^{3-}$ was first optimized, where this compound was recently crystallized by Cross et al.[4] In their crystal structures, the average Am−Cl bond distance was reported to be 2.724 Å. Our calculations indicated an average bond distance of 2.833 Å, which deviates slightly from the experimental data. This difference is due to the limitations of the computations, where the calculated structures are optimized in the gas phase and the polarization effects of the crystal structure are ignored. The same level of theory was applied for the calculation of the optimized structures of $Am(H_2O)_9$ and $Am(Ox)_n \cdot (H_2O)_{9\text{-}2n}$ (n = 1–3) illustrated in Fig. 7. The optimized structures had negligible spin contamination in the unrestricted DFT ground states, where the $<S^2>$ values were close to the ideal value of $S(S+1)$.

Characterization of bonding strength between Am(III) and O of water (O_w) by NBO calculations To characterize the interactions between Am(III) and water molecules in the first sphere, NBO study was conducted. As summarized in Table S5, the lone pair electrons in p orbitals of O_w is donating some amount of electron to the d and/or f orbital of Am(III) (Table S6). The calculated highest second-order interaction energy (E^2) in each bonding between O_w and Am(III) orbitals is decreasing sequentially as Am(III) forms complexes with Ox ligands (from 7.13-18.69 to 1.3-4.28 kcal/mol). The results indicate that Am(III)-Ox complex with bidentate structure in solution shortens the Am-O_{Ox} bond distance, whereas, lengthen the Am-O_w bond distances by weaker bonding strength.

Table S5. NBO analysis of Am-O_w, their description and highest second-order interaction energies between donor (p orbital of Oxygen in water) and acceptor (d/f orbitals of Americium in each complex)

	Donor atom	NBO donor orbital	Description of donor orbital	Acceptor atom	NBO acceptor orbital	Description of acceptor orbital	E^2(kcal/mol)
Am(H$_2$O)$_9$	O1	LP (O)	p(100%)	Am	LP*(Am)	s(0.17%)p(2.65%)d(95.06%)f(2.12%)	18.69
	O2					s(0.11%)p(3.41%)d(96.35%)f(0.12%)	8.94
	O3					s(0.02%)p(2.43%)d(92.07%)f(5.47%)	9.76
	O4					s(0.02%)p(2.43%)d(92.07%)f(5.47%)	7.13
	O5					s(0.49%)p(4.13%)d(94.75%)f(0.63%)	12.28
	O6					s(0.06%)p(90.00%)d(8.64%)f(1.30%)	9.39
	O7					s(0.73%)p(13.27%)d(85.13%)f(0.88%)	12.52
	O8					s(0.11%)p(3.41%)d(96.35%)f(0.12%)	11.25
	O9					s(0.78%)p(91.53%)d(6.52%)f(1.16%)	10.88
Am (Ox)$_1$(H$_2$O)$_7$	O1	LP (O)	p(100%)	Am	LP*(Am)	s(52.08%)p(5.63%)d(41.89%)f(0.40%)	5.07
	O2					s(0.64%)p(4.29%)d(93.82%)f(1.25%)	1.27
	O3					s(0.64%)p(4.29%)d(93.82%)f(1.25%)	11.42
	O4					s(0.14%)p(55.18%)d(41.36%)f(3.31%)	1.17
	O5					s(0.64%)p(4.29%)d(93.82%)f(1.25%)	1.49
	O6					s(0.38%)p(1.54%)d(97.83%)f(0.25%)	11.81
	O7					s(0.38%)p(1.54%)d(97.83%)f(0.25%)	6.23
Am (Ox)$_2$(H$_2$O)$_5$	O1	LP (O)	p(100%)	Am	LP*(Am)	s(2.74%)p(6.01%)d(87.52%)f(3.73%)	1.18
	O2					s(0.24%)p(12.38%)d(85.91%)f(1.47%)	1.98
	O3					s(0.24%)p(12.38%)d(85.91%)f(1.47%)	10.67
	O4					s(0.48%)p(74.35%)d(24.78%)f(0.39%)	1.07
	O5					s(0.05%)p(90.21%)d(8.35%)f(1.38%)	0.57
Am (Ox)$_3$(H$_2$O)$_3$	O1	LP (O)	p(100%)	Am	LP*(Am)	s(0.00%)p(0.51%)d(84.85%)f(14.64%)	4.28
	O2					s(0.00%)p(0.00%)d(0.03%)f(99.97%)	1.3
	O3					s(0.15%)p(2.16%)d(96.09%)f(1.60%)	3.52

Hydrogen bonding interactions between oxalate and water molecules To understand why O_w atoms in the Am-Ox complexes are not oriented toward Am(III) center, we investigated the hydrogen bonding properties between water and oxalate in the complexes by calculating core-valence bifurcation (CVB) index, which have been frequently used to estimate the hydrogen bond strength on the basis of electron localization function.[5] CVB index is positive for weak hydrogen bond and it decreases with stronger hydrogen bond; usually its negative index stands for the strong hydrogen bonds.

Am (Ox)$_1$(H$_2$O)$_7$ Am (Ox)$_2$(H$_2$O)$_5$ Am (Ox)$_3$(H$_2$O)$_3$
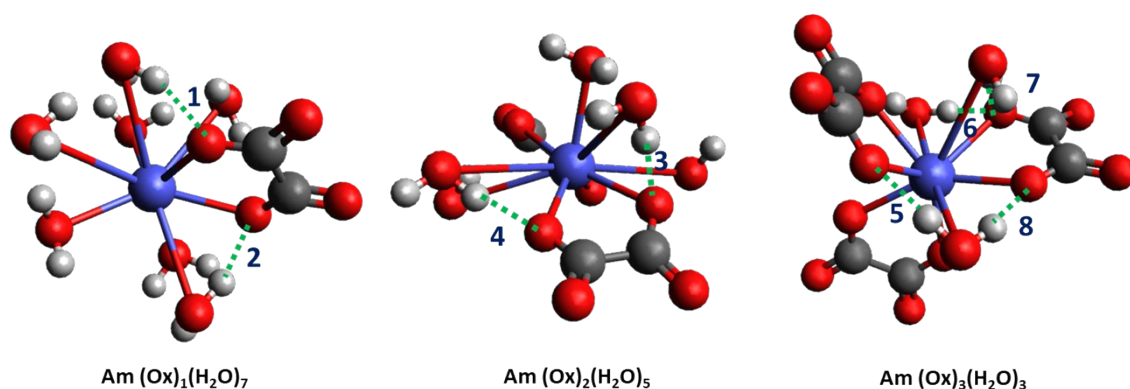
Strong hydrogen bonding formation between water and oxalate

	Bond Length	CVB index
1	1.87	-0.0081
2	1.94	-0.0009
3	1.76	-0.0414
4	1.85	-0.0270
5	1.92	0.0027
6	1.88	-0.0875
7	1.91	-0.0153
8	1.96	0.0159

Figure S3. Selected hydrogen bonding property studies on the optimized Am-Ox structures by CVB index, an indicator on the strength of hydrogen bond.

Analysis of electronic structure of Am(III) All electronic structure analyses including natural population analysis (NPA) charges were performed using natural bond orbital (NBO) calculations. The multiplicity for each studied complex was determined from the lowest energy states by comparing energies of all possible spin states. The Am(III) charges, electron configurations, and spin densities for each complex are summarized in Table S6.

All the studied complexes favor the identical spin multiplicity of septet as the lowest-energy state. In the spin population shown in Table S5, the unpaired electrons are predominantly derived from the 5f-electron contributions. All the other contributions from 7s, 6d, and 7p are less than 1 electron. According to the predicted NPA charges of Am(III), Am(III) in all studied complexes is acting as an electron acceptor and one can conclude that the 7s, 6d, and 7p orbitals are additionally occupied by electrons from ligands by forming chemical bonds with organic ligands. This is confirmed by the decrease in positive charge and the retention of the 5f^6 orbital structure.

Table S6. Electron structures of Am(III) in the studied complexes are predicted by calculating the energies of all spin states and analyzing NPA charge values with NBO investigation.

Complexes	Multiplicity	Charge on Am	Electron Configuration	Spin Density
Am(III)		3	$5f^6$	NC
Am(H$_2$O)$_9$		1.69	$7s^{0.25}5f^{6.09}6d^{0.57}7p^{0.22}$	$5f^{5.98}6d^{0.03}$
Am(H$_2$O)$_7$(Ox)$_1$	7	1.68	$7s^{0.235}5f^{6.22}6d^{0.587}7p^{0.22}$	$7s^{0.01}5f^{5.98}6d^{0.03}$
Am(H$_2$O)$_5$(Ox)$_2$		1.79	$7s^{0.25}5f^{6.15}6d^{0.57}7p^{0.01}$	$7s^{0.01}5f^{5.98}6d^{0.03}$
Am(H$_2$O)$_3$(Ox)$_3$		1.61	$7s^{0.21}5f^{6.10}6d^{0.69}7p^{0.38}8s^{0.02}$	$7s^{0.01}5f^{5.97}6d^{0.04}7p^{0.01}$

NC: not calculated because it is obviously $5f^6$

Electronic topology analysis suggests ionic bonding properties between Am(III) and O of Ox (O$_{Ox}$) To understand more about the nature of the bonding properties of the Am-O$_{Ox}$, we performed electron topology analysis using Bader's atoms-in-molecule (AIM) bond critical point analysis (a sample of bond critical points (3, -1) are represented in Figure S3). Bonding property index (BPI) is defined as negative potential energy density, V(r), divided by the Lagrangian kinetic energy, G(r). A value less than 1 for the -V(r)/G(r) ratio indicates a typical ionic bond, while a value greater than 2 represents covalent bonding.

Based on this information, one can conclude that Am(III)-Ox complexes, whose average BPI is less than 1, contain mostly ionic bonds. This is an expected result in conjunction with Wiberg bond indices (WBI) analysis and NPA charge calculation; the negatively charged oxalate ligand provides a large population of electrons to positively charged Am(III), which results in the ionic bonding properties. Additionally, the electron density and Laplacian of electron density were calculated. Generally, the electron density in a bond critical point is used as a standard of bonding properties, where more ionic bonding gives a smaller electron density and larger Laplacian of electron density. As presented in Figure S3, these data also represent the formation of stronger ionic bonding in Am(III)-Ox complexes.
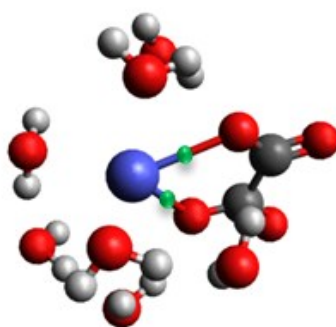
	(3, -1)bond critical point				
	Electron density	Laplacian of electron density			-V(r)/G(r)
	average	std	average	std	average
$Am(H_2O)_7(Ox)_1$	0.045	0.005	0.181	0.031	0.991
$Am(H_2O)_5(Ox)_2$	0.044	0.004	0.179	0.022	0.990
$Am(H_2O)_3(Ox)_3$	0.043	0.004	0.174	0.023	0.993

Figure S4. $Am(H_2O)_7(Ox)_1$ structure describing the bond critical point (3, -1) with green dots (upper picture) and the calculated bond property indices with electron density and the Laplacian of electron density are tabulated.

References

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Structural coordination of Am-oxalates

Am(H₂O)₉

Am	-0.03558600	0.77848100	-0.14581700
O	2.15557300	2.22613000	-0.11613200
H	2.79702400	1.57424400	0.21848000
O	1.75089200	-0.19394700	-1.99906800
H	1.88012500	-1.10875500	-1.69507900
H	2.46802500	2.43705600	-1.01290700
H	2.59139100	0.24508700	-1.78267600
O	-0.09193400	2.54442400	1.96326100
H	-0.70180400	2.11819000	2.58949300
O	-0.41079400	2.61651800	-1.93510500
H	-0.35642200	2.23571800	-2.82891400
O	-0.06140100	-2.04228600	-0.14175200
H	-0.49938900	-2.08673300	0.72641700
O	1.73360400	-0.17028600	1.75483800
H	1.40336400	0.32623600	2.52411300
O	-1.89079400	-0.17653200	1.67995500
H	-2.38954100	0.63245900	1.43191900
O	-1.86214300	-0.17961100	-1.97818400
H	-1.82882000	0.44309300	-2.72414000
O	-2.47871100	2.16716500	0.27665500
H	-2.37936800	3.06079900	0.64571800
H	-1.36265000	2.76051700	-1.78406600
H	-1.57762700	-0.00129200	2.58352300
H	0.83469700	-2.38233800	0.02454400
H	1.35591800	-1.05897300	1.87596100
H	-1.42269400	-0.97819300	-2.31763100
H	-3.18159500	2.24475600	-0.39081600
H	0.76147600	2.55395700	2.42907900

Am(H₂O)₇(Ox)₁

Am	-0.26969900	0.90661000	-0.45882800
O	1.99753500	2.07213500	-0.21907500
O	2.17986100	0.37017500	-2.55712400
H	1.82477300	0.95702800	-3.24557900
H	2.30037800	0.97600400	-1.79703700
O	-0.18982600	2.89374100	2.04119800
H	-0.02597800	1.95927400	2.26271700
O	0.02046500	2.78210400	-2.30655500
H	0.97621200	2.92714400	-2.18104500
O	-1.74214700	-2.37115200	0.22278800
H	-1.66272100	-1.70582900	0.95248700
O	1.18620300	-0.05126800	1.24104900
O	-1.39130700	-0.49270100	2.25410800
H	-1.73841100	0.36341100	1.94710100
O	-1.42735100	-0.84962600	-1.98919700
H	-0.69943500	-1.23259800	-2.50907100
O	-2.32075900	2.41592000	0.34476300
H	-1.73470300	2.71170000	1.08493100
H	-0.04894000	2.40412600	-3.20064000
H	-0.41916500	-0.39138300	2.14644600
H	-0.90791000	-2.86840300	0.26810700
H	-1.58534600	-1.50258800	-1.24995900
H	-3.02549200	1.89805800	0.77059800
H	0.48046500	3.06690400	1.35370500
C	2.81080000	1.67379100	0.70219600
C	2.32789100	0.46097700	1.57154400
O	3.91781900	2.17023300	0.95233800
O	3.04457500	0.06945300	2.50056800

Am(H₂O)₅(Ox)₂

Am	0.48737500	0.90465600	-0.02822900
O	2.75249400	1.81875800	-0.06777900
O	2.24429000	1.03978300	-2.80174900
H	1.30696400	1.32609000	-2.79922900
H	2.59044300	1.40572100	-1.96342000
O	0.11784100	2.08483400	2.98701800
H	-0.74827500	1.63758800	2.83461900
O	0.16205000	-1.65166700	-0.37346800
H	-0.15986600	-1.99859500	0.47642500
O	1.90326400	0.12039100	1.84674700
O	-2.33798100	0.91024400	2.30894700
H	-2.30146800	1.44555500	1.47859300
O	-1.90481800	-0.92586000	-1.94556900
H	-1.42661700	-0.08581700	-2.13811100
H	-2.95420100	1.39604800	2.88277400
H	-0.65607400	-1.53428200	-0.93221300
H	-2.58719200	-0.65201500	-1.30838300
H	0.77138900	1.38173400	2.80102300
C	3.65072000	1.41673800	0.76695900
C	3.14266200	0.47646200	1.91438700
O	4.85345500	1.71293800	0.72943700
O	3.94520200	0.13504700	2.79535700
O	-1.70315400	2.19819100	-0.00103800
O	-0.50155000	1.50443800	-2.31419900
C	-2.24576400	2.63564200	-1.08218100
C	-1.40538400	2.42907900	-2.38254300
O	-3.35021600	3.19429700	-1.17267300
O	-1.65875300	3.11960100	-3.37817400

Am(H₂O)₃(Ox)₃

Am	-0.01113600	0.42880700	-0.29197200
O	2.43335900	1.36776500	0.11072100
O	2.14535600	0.98562800	-2.66755200
H	1.34045900	1.54117200	-2.63484500
H	2.47196900	1.05981000	-1.74594500
O	0.68850600	3.35585200	1.20951600
H	0.33948200	2.71301800	1.85022300
O	0.82472300	0.40904800	2.05967100
O	-2.05505700	0.08030600	2.20353500
H	-2.24760500	0.75015300	1.51544700
H	-1.10140700	0.20620200	2.37605600
H	1.33636500	2.79977400	0.72588400
C	3.02168000	0.93908700	1.17501500
C	2.07437800	0.50258400	2.35134800
O	4.24810200	0.84575800	1.34311200
O	2.58152400	0.27400900	3.46174800
O	-2.17503100	1.70100400	-0.15049700
O	-0.24989300	2.32962600	-1.92316600
C	-2.28927900	2.84716700	-0.72183600
C	-1.18560500	3.19693800	-1.78394400
O	-3.18672700	3.67936800	-0.50549100
O	-1.28972700	4.26906300	-2.40615900
O	-1.27624100	-0.60760300	-2.15897700
O	0.25240300	-2.02245200	-0.46145900
C	-1.19848200	-1.86769000	-2.39403600
C	-0.28914200	-2.68984700	-1.41761500
O	-1.77516800	-2.47340400	-3.31570800
O	-0.14855700	-3.90887300	-1.62170000