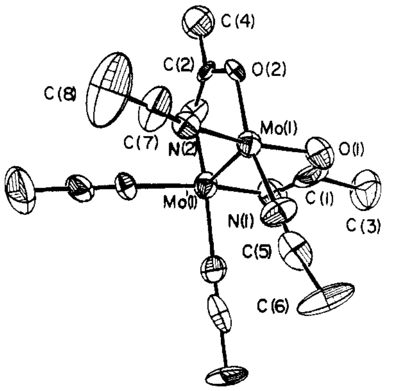

Figure 2. ORTEP diagram of the cation in **2**. Each atom is represented by its ellipsoid of thermal vibration at the 50% probability level. The axial triflate groups have been omitted for clarity.

Table VII. Selected Bond Angles (deg) for *cis*-$[Mo_2(O_2CCH_3)_2(CH_3CN)_4(O_3SCF_3)_2](HO_3SCF_3)_2(THF)$

Mo(1)-Mo(1)-N(1)	103.04 (48)	Mo(1)-O(1)-C(1)	119.56 (165)
-N(2)	103.32 (56)	-O(2)-C(2)	111.88 (185)
-O(1)	89.39 (48)	-N(1)-C(5)	171.97 (208)
-O(2)	91.20 (49)	-N(2)-C(7)	176.86 (230)
-O(3)	170.51 (41)	N(1)-C(5)-C(6)	175.46 (346)
N(1)-Mo(1)-O(1)	90.75 (54)	N(2)-C(7)-C(8)	170.62 (298)

CH_3CN ligands, 2.132 (10) and 2.137 (10) Å, are similar to the Mo–O distances, 2.068 (7) and 2.079 (7) Å, whereas the axial Mo–N distances are very long, 2.64 (2) and 2.77 (2) Å. These latter long distances are in accord with the possibility of easy dissociation of the axial ligands.

The $[Mo_2(O_2CCH_3)_2(CH_3CN)_4(ax\text{-}O_3SCF_3)_2]^{2+}$ cation of **2** possesses a crystallographic mirror plane that bisects the metal–metal bond. The structure is depicted via the ORTEP diagram given in Figure 2. Positional parameters are given in Table V. Distances and angles are listed in Tables VI and VII. The distances and angles within the cation of **2** are identical with those within **1** within experimental error. The axial CF_3SO_3 anions represent the first reported example of axially coordinated triflate groups attached to a quadruple bond. The Mo–O(ax) distance is 2.576 (15) Å, with the Mo–Mo–O(ax) angle being 170.51 (41)°. There is an infinite chain of O–S–O–Mo–Mo–O–S–O linkages throughout the crystal.

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Registry No. 1, 98542-25-7; **2**, 98542-27-9; $Mo_2(O_2CCH_3)_4$, 14221-06-8; Mo, 7439-98-7; $(C_2H_5)_3OBF_4$, 368-39-8.

Supplementary Material Available: Details of the crystallographic procedures and tables of observed and calculated structure factors and anisotropic thermal parameters for **1** and **2** and a listing of complete bond lengths and angles for **1** (19 pages). Ordering information is given on any current masthead page.

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Calorimetric Studies of Curium Complexation

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The high specific radioactivity of the common isotopes of the transplutonium elements has been a major deterrent to study of their complexation reactions by methods that require macroconcentrations of the metal ions. Radiotracer distribution techniques are satisfactory for measurement of stability constants although, in general, values of the enthalpies of complexation and, consequently, of the entropies of complexation obtained from such distribution measurements at different temperatures are less reliable.

Curium samples have become available with a relatively low specific activity (ca. 3 × 10^7 α decays/(m·mg)) due to a high isotopic content, 96.9%, of ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ y). With use of milligram quantities of this material, direct calorimetric measurements could be made in the minicalorimeter[2] of the Florida State University Laboratory. The systems Cm + OAc (acetate) and Cm + EDTA (ethylenediaminetetraacetate) were chosen for study as these ligands form relatively weak (OAc) and very strong (EDTA) complexes.

Formation of transplutonium cation complexes with acetate has been investigated by a solvent extraction method over a temperature range of 0 to 55 °C.[3] The stability constants at 24 °C agreed well with the lanthanides of similar ionic radii, but the enthalpy and entropy values of the actinides were significantly more positive than those of the lanthanides. It was suggested that this might reflect more dehydration of the trivalent actinides upon complexation; however, the authors noted that the results were questionable as they were obtained by temperature variation.

The thermodynamics of complexation of Pu(III) and Am(III) by EDTA was studied by calorimetry[4] with samples of crystalline $PuCl_3$ and $AmCl_3$ dissolved in EDTA solutions. Suitable corrections for enthalpies of solution and of deprotonation were required. A measurement of $LaCl_3$ by the same technique gave a value of ΔH of complexation that did not agree well with direct solution calorimetric measurements,[5] casting doubt on the actinide values. A more recent study used solvent extraction at different temperatures and reported rather different values of ΔH and ΔS.[6]

Experimental Section

Chemicals. Solutions of $Eu(ClO_4)_3$, HCl, NaOH, $NaClO_4$, Na_2H_2EDTA, and HOAc were prepared from reagent or analytical grade chemicals in distilled, deionized water. The NaOAc buffer solution was prepared from HOAc by adjustment of the pH with NaOH solution. The ionic strength of the solution was adjusted with $NaClO_4$ to 2.0 M for the Cm + OAc titration and to 0.5 M for the Cm + EDTA runs. These values were chosen to allow comparison with literature data.

The 6.05 mg of curium was received as dry $CmCl_3$ from Oak Ridge National Laboratory. The sample was dissolved by gentle warming in 0.5 mL of 0.0409 M NH_4Cl, pH 5.83. Assay of the α decay by liquid scintillation counting confirmed that 6.0 ± 0.1 mg of Cm had been dissolved.

Procedure. The curium solution was transferred to the calorimeter cup and 4.00 mL of 2.186 M $NaClO_4$ solution added to produce a 2.00 M ($NaClO_4$) ionic strength solution of pH ca. 5.8. This solution was titrated automatically by incremental additions of a solution of acetate that was 0.02 M in HOAc, 0.08 M in NaOAc, and 2.0 M in $NaClO_4$. The procedures for operation of the computer-operated calorimetric titration have been described earlier.[7]

After the acetate experiment, the solution in the calorimeter cup was removed and made basic with NaOH to precipitate $Cm(OH)_3$; analysis of the supernatant after warming and centrifugation indicated that 2–5% of the Cm had not precipitated. The precipitate was washed and, then, dissolved in 0.5 mL of 0.552 M NH_4Cl solution to give a pH of 5.34. This solution was added to the calorimeter cup with 0.002 mL of 4 M

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Table I. Data for the Calorimetric Titrations of Eu(III) and Cm(III)[a]

titrant addition, mL	ΔQ, J			
	Eu + Ac	Cm + Ac	Eu + EDTA	Cm + EDTA
0.10	0.013 55	0.01 62	0.068 69	0.057 24
0.20	0.011 99	0.01 16	0.074 29	0.053 94
0.30	0.009 74	0.00 84	0.069 59	0.051 24
0.40	0.008 07	0.00 92	0.067 69	0.051 34
0.50	0.010 37	0.00 93	0.069 09	0.054 34
0.60	0.007 25	0.00 74	0.066 79	0.051 54
0.70	0.003 97	0.00 49	0.064 49	0.045 54
0.80	0.004 08	0.00 48	0.061 39	0.036 94
0.90	0.006 44	0.00 598	0.064 99	0.027 94
1.00	0.002 93	0.00 450	0.054 39	0.015 04
1.10	0.004 08	0.00 410	0.042 39	0.010 84
1.20	−0.000 02	0.00 030	0.027 29	0.007 44
1.30	0.003 50	0.00 570	0.020 69	0.004 64
1.40	0.001 93	0.00 571	0.009 39	0.006 84
1.50	0.001 54	0.00 450	0.005 39	0.003 54
1.60	0.002 31	0.00 270	0.001 19	0.001 94
1.70	0.002 56	0.00 300	0.000 59	−0.000 26
1.80	0.002 25	0.00 300	−0.001 51	−0.000 16
1.90	0.002 38	0.00 372	−0.001 51	−0.000 96
2.00	0.001 16	0.00 150	−0.003 81	−0.000 56

[a] I = 2.0 M ($NaClO_4$) for acetate; I = 0.5 M ($NaClO_4$) for EDTA.

HCl and 4.00 mL of 0.453 M $NaClO_4$ to produce an ionic strength of 0.50 M. The titrant was a solution of 0.025 M Na_2H_2EDTA at pH 5.00 and ionic strength 0.50 M ($NaClO_4$).

Similar titrations of Eu(III) were conducted, in order to check the validity of the curium data, for comparison with the ΔH values of $EuOAc^{2+}$ and $EuEDTA^-$ reported in the literature.[8]

Data Analysis. The data from the calorimetric titrations were analyzed with the ET program[9] on the Z-80 microcomputer of the FSU laboratory. For the acetate titrations, the curium concentration in the cup was assumed to be 0.00542 M (6.05 mg of Cm) and the ΔH of reaction calculated by the program. The curium concentration was found to be 0.00481 M (5.37 mg of Cm) in the EDTA titration. The Eu(III) concentration was 0.00481 M in the EDTA titration and 0.00594 M for the acetate experiments.

Results

Table I gives the primary titration data for curium and europium with acetate and EDTA. The ΔQ values have been corrected for base line and heats of dilution.

The calorimetric titration with EDTA corresponded to the reaction

$$M^{3+} + H_2EDTA^{2-} = M(EDTA)^- + 2H^+$$

To convert to the direct reaction

$$M^{3+} + EDTA^{4-} = M(EDTA)^-$$

it was necessary to correct the measured ΔH value for formation of CmEDTA by the deprotonation enthalpy of H_2EDTA^{2-} at 0.50 M ($NaClO_4$) ionic strength, which has been reported to be −51.8 ± 0.3 kJ·m^{-1}.[8]

Table II lists the calculated enthalpy values of the curium and europium titrations for the reaction of M + L = ML (L = OAc, EDTA). The results of a second Eu(III) + OAc titration conducted after the EDTA runs are also included.

Table II. Thermodynamic Parameters of Cm(III) and Eu(III) Complexation (T = 25.00 °C)

metal	ΔH, kJ·m^{-1}	ΔG, kJ·m^{-1}	ΔS, J·m^{-1}·K^{-1}
	Acetate [I = 2.0 M ($NaClO_4$)]		
Cm	5.95 ± 0.42	−11.68 ± 0.13[a]	57 ± 2
Eu (1)	5.87 ± 0.43	−10.93 ± 0.05[a]	56 ± 2
Eu (2)	6.20 ± 0.48		58 ± 2
	EDTA [I = 0.50 M ($NaClO_4$)]		
Cm	−29.3 ± 1.3	−96.2 ± 0.5[b]	225 ± 6
Eu	−22.9 ± 1.3	−92.6 ± 0.4[c]	234 ± 6

[a] Reference 3. [b] Reference 6. [c] Reference 8.

Discussion

The values of ΔH and ΔS for $CmOAc^{2+}$ formation in Table II differ substantially from the values (+18.0 ± 0.8 kJ·m^{-1} and 100 ± 3 J·m^{-1}·K^{-1}, respectively) in ref 3. The values for formation of $EuOAc^{2+}$ in ref 3 are −5.9 ± 0.4 kJ·m^{-1} (ΔH) and 56 ± 2 J·m^{-1}·K^{-1} (ΔS), which agree well with the values in Table II. No explanation is apparent for the temperature variation method failing for the Cm system but succeeding for the Eu system in the study in ref 3. However, the direct calorimetric values in Table II seem valid and indicate a strong similarity in the behaviors of the trivalent actinides and lanthanides in complexation with acetate anions. The difference in cation dehydration proposed in ref 3 is not evident in our data.

For the EDTA complexation, the only comparable calorimetric datum is for formation of $AmEDTA^-$ at I = 0.1 M for which the reported enthalpy is ΔH = 19.5 ± 1.0 kJ·m^{-1}.[4] In that work, the enthalpy of formation of $LaEDTA^-$ was measured also and a value of ΔH = −4.8 ± 8 kJ·m^{-1} obtained. This is 8.3 kJ·m^{-1} more endothermic than the value in ref 5, which reports later and more sensitive work. Moreover, the ΔH value for $LaEDTA^-$ obtained in this laboratory[8] at I = 0.5 M is −15.6 kJ·m^{-1}, which, considering the difference in ionic strength, agrees well with that of ref 5. Correcting the $AmEDTA^-$ enthalpy by the difference in the enthalpy values for $LaEDTA^-$ of ref 4 and 8, −11.8 kJ·m^{-1}, results in a value of ΔH = −31.2 ± 2.2 kJ·m^{-1}, which agrees with that reported in ref 6 from measurement of log β_{101} at different temperatures. That study also reported a value of ΔH = −29 ± 2 kJ·m^{-1} for $CmEDTA^-$. The agreement of this latter value as well as that for $AmEDTA^-$ with our value in Table II provides strong support for the validity of the latter. The agreement between the $EuEDTA^-$ data in Table II (ΔH = 24.9 ± 0.3 kJ·m^{-1}) and that in ref 8 (ΔH = 24.9 ± 0.3 kJ·m^{-1}) is further support. Again, the similarity in complexation thermodynamics between trivalent lanthanides and actinides is evident.

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Back-Bonding Effects of Osmium(III): Crystal Structure of (μ-Pyrazine)decaamminediosmium(III) Chloride Dihydrate

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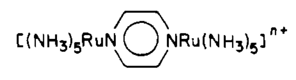
Since the initial reports of pyrazine- (pyz-) bridged binuclear ions of ruthenium ammines,[1] I, many binuclear ruthenium com-



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plexes have been prepared and characterized.[2-4] However, the electronic structure of the mixed-valence ruthenium complex

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