

Sodium tris(acetato- κ^2O,O')dioxidoamericatate(VI) and guanidinium tris(cyclopropanecarboxylato- κ^2O,O')dioxidoamericatate(VI)

Mikhail S. Grigoriev* and Alexandre M. Fedosseev

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Leninsky Prospekt, 119991 Moscow, Russian Federation
Correspondence e-mail: mickgrig@mail.ru

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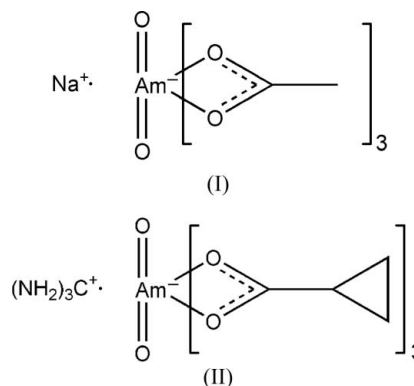
The title compounds, $\text{Na}[\{\text{AmO}_2\}(\text{C}_2\text{H}_3\text{O}_2)_3]$, (I), and $(\text{CH}_6\text{N}_3)[\{\text{AmO}_2\}(\text{C}_4\text{H}_5\text{O}_2)_3]$, (II), contain complex anions in which AmO_2^{2+} cations are surrounded by three bidentate-chelating carboxylate groups. The atoms of the AmO_2 group and the Na atoms in (I) are situated on threefold axes. All the atoms in (II) occupy general positions. Both compounds are isomorphous with earlier studied analogous compounds of previous members of the actinide (An) series.

Comment

Linear dioxidocations AnO_2^+ and AnO_2^{2+} are typical of actinides (An) in oxidation states V and VI. Most of the crystal structures reported for compounds containing such cations involve U^{VI} and Np^{V} . The data for Pu compounds are more scarce. Am^{VI} compounds are usually believed to be isomorphous with corresponding compounds of U, Np and Pu. Nevertheless, there are several examples of Pu^{VI} compounds that are not isomorphous with their U and Np analogues. Pu^{VI} orthophthalate $\{\text{PuO}_2[(\text{OOC})_2\text{C}_6\text{H}_4]\text{H}_2\text{O}\} \cdot \text{H}_2\text{O}$ (Grigoriev *et al.*, 2004) is not isomorphous with $\{\text{UO}_2[(\text{OOC})_2\text{C}_6\text{H}_4]\text{H}_2\text{O}\} \cdot \text{H}_2\text{O}$ (Charushnikova *et al.*, 2004). In this case, the change in the coordination mode of the phthalate anion (seven-membered metallocycle in the U compound and four-membered metallocycle in the Pu compound) can be explained by a decrease in the ionic radius on going from U to Pu, *viz.* the actinide contraction (Edelstein *et al.*, 2006). $[(\text{PuO}_2)_2\text{SiO}_4(\text{H}_2\text{O})_2]$ crystallizes in a tetragonal space group whereas its U and Np analogues crystallize in an orthorhombic one (Grigor'ev *et al.*, 2003; Bessonov *et al.*, 2003). In the case of $[\text{PuO}_2(\text{IO}_3)_2] \cdot \text{H}_2\text{O}$ and $[\text{UO}_2(\text{IO}_3)_2(\text{H}_2\text{O})]$, even the composition of the coordination polyhedron is different (Bean *et al.*, 2001; Runde *et al.*, 2003).

Until recently, full X-ray crystallographic data for Am^{VI} compounds have not been available. We present here two crystal structure determinations for Am^{VI} tricarboxylate com-

plexes, *viz.* sodium tris(acetato- κ^2O,O')dioxidoamericatate(VI), $\text{Na}[\text{AmO}_2(\text{OOCCH}_3)_3]$, (I), and guanidinium tris(cyclopropanecarboxylato- κ^2O,O')dioxidoamericatate(VI), $[\text{C}(\text{NH}_2)_3][\text{AmO}_2(\text{OOCCH}_2\text{C}_3\text{H}_5)_3]$, (II).



Several structure determinations for $\text{Na}[\text{AnO}_2(\text{OOCCH}_3)_3]$ compounds have been reported (Zachariassen & Plettinger, 1959; Alcock *et al.*, 1982; Templeton *et al.*, 1985; Navaza *et al.*, 1991; Charushnikova *et al.*, 2007). For the Am compound, only unit-cell constants have been determined and the isostructurality with other An^{VI} compounds has been shown (Jones, 1955). Only a brief description is available for the crystal structure of $[\text{C}(\text{NH}_2)_3][\text{NpO}_2(\text{OOCCH}_2\text{C}_3\text{H}_5)_3]$ (Andreev *et al.*, 2006).

Both title compounds contain complex anions in which AmO_2^{2+} cations are surrounded by three bidentate-chelating carboxylate anions (Figs. 1 and 2). The atoms of the AmO_2 group and Na atoms in (I) occupy special positions $4a$ in the space group $P2_13$ on threefold axes. All the atoms in (II) occupy general positions. The coordination polyhedra of the Am atoms in both compounds are distorted hexagonal bipyramids with the two O atoms of the AmO_2 groups in apical positions and six O atoms from three carboxylate

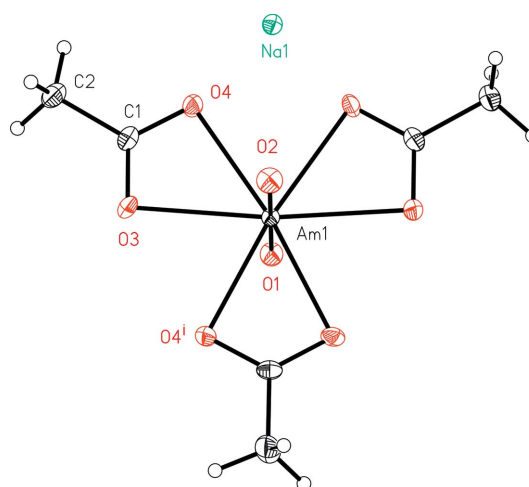
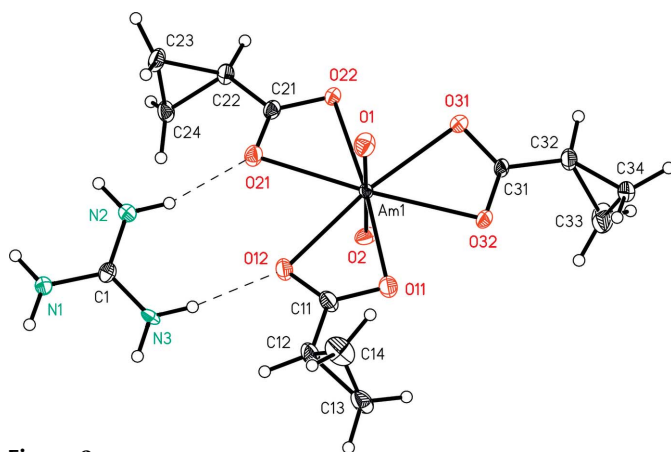


Figure 1
A view of the components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. [Symmetry code: (i) y, z, x .]


Figure 2

A view of the components of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Dashed lines indicate the hydrogen-bonding interactions.

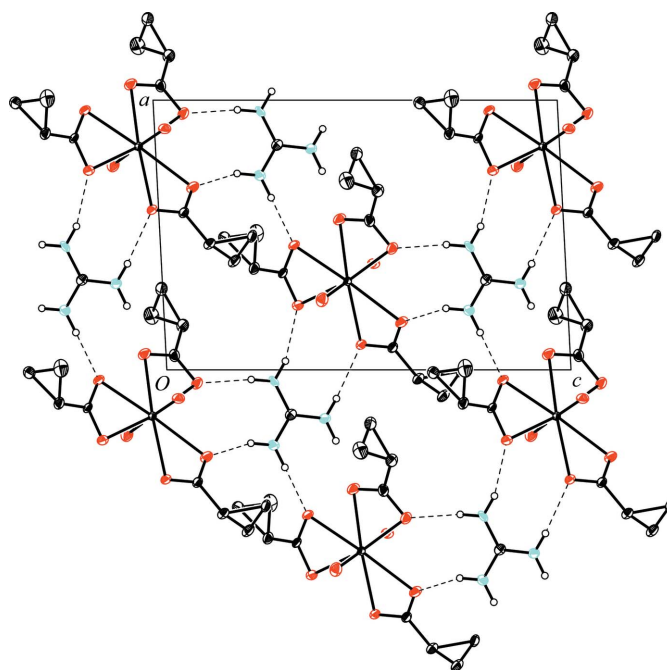
groups in equatorial positions. The main distortion of the polyhedra is the difference between O—Am—O angles for O atoms of the same carboxylate group and for O atoms of two different carboxylate groups, these values being about 53 and 67°, respectively (Tables 1 and 2). The AmO₂ groups, ideally linear in (I) and almost linear in (II), are almost symmetric with close average Am—O distances of 1.738 (9) and 1.745 (4) Å, respectively. The average Am—O distances in the equatorial planes of the AmO₂ groups are 2.460 (5) and 2.461 (4) Å for (I) and (II), respectively.

The coordination polyhedron of the Na atom in (I) can be described as a strongly distorted octahedron, formed by carboxylate O atoms, with three Na—O distances of 2.358 (5) Å and three distances of 2.384 (6) Å.

The guanidinium cations in (II) act as proton donors in several hydrogen bonds (Fig. 3 and Table 3) with O atoms of the carboxylate groups of the organic anions. Each cation is connected to three complex anions forming layers parallel to the (010) plane.

Both compounds are isomorphous with earlier studied analogous compounds of previous members of the actinide series. The average An—O distances in Na[AnO₂(OOCCH₃)₃] compounds are (in AnO₂ groups and in their equatorial planes, respectively) 1.758 and 2.464 Å for U (Templeton *et al.*, 1985), 1.776 (7) and 2.456 (12) Å for Np (Alcock *et al.*, 1982), and 1.736 (8) and 2.462 (5) Å for Pu (Charushnikova *et al.*, 2007). The An—O distances in the equatorial plane of the AnO₂ groups are practically the same in all compounds. The An=O distances in the AnO₂ groups differ more significantly but without any pronounced trend. In contrast, a general decrease in the An=O distances in the AnO₂ groups with increasing atomic number of the An atom was found for (NH₄)[AnO₂(CO₃)₃] compounds (An = U, Np, Pu; Charushnikova *et al.*, 2007).

The Np—O distances in [C(NH₂)₃][NpO₂(OOCCH₃)₃] (Andreev *et al.*, 2006) are 1.744 (5) and 1.752 (5) Å in the NpO₂ group and range from 2.437 (5) to 2.497 (5) Å in the equatorial plane, close to the values found in (II).


Figure 3

The pattern of hydrogen bonding in (II). The H atoms of the cyclopropanecarboxylate anions have been omitted for clarity.

Thus, this study has proved the isomorphism of (I) and (II) with analogous compounds of previous members of the actinide series. The main difference in interatomic distances is some shortening of An—O bonds in AnO₂ groups in (I) and its analogues in the U—Np—Pu—Am sequence.

Experimental

²⁴³Am(NO₃)₃ with a negligible admixture of ²⁴¹Am was used as the starting material for the syntheses of (I) and (II). Brown-yellow crystals of (I) were obtained by neutralization of Am^{VI} (5×10^{-3} M) in NaHCO₃ solution (0.1 M), prepared by ozonation of the initial Am^{III} suspension in NaHCO₃ (0.1 M), and excess of an aqueous CH₃COOH solution (1 M). Crystallization commences in such solutions within a few minutes but usually the crystals are rather small.

Light-brown-yellow crystals of (II) were obtained by slow evaporation of a solution containing Am^{VI} (5×10^{-3} M) and guanidinium cyclopropanecarboxylate (0.1 M). This solution was prepared by ozonation for about 15 min of a suspension, obtained by addition of an Am(NO₃)₃ solution (0.1 ml, 2×10^{-2} M) to guanidinium carbonate (0.4 ml, 0.11 M), and with subsequent addition of a freshly prepared water solution (0.05 ml) of cyclopropanecarboxylic acid (1 M).

Compound (I)

Crystal data

Na[Am(C₂H₃O₂)₃O₂]
M_r = 475.12
 Cubic, *P*2₁3
a = 10.5967 (2) Å
V = 1189.90 (4) Å³

Z = 4
 Mo *K*α radiation
 μ = 6.51 mm⁻¹
T = 100 K
 0.04 × 0.04 × 0.04 mm

Table 1
Selected geometric parameters (Å, °) for (I).

Am1—O1	1.735 (9)	Am1—O3	2.464 (5)
Am1—O2	1.742 (9)	Am1—O4	2.455 (5)
O1—Am1—O2	180.00	O4 ⁱ —Am1—O3	67.26 (16)
O3—Am1—O4	52.74 (16)		

Symmetry code: (i) y, z, x .

Table 2
Selected geometric parameters (Å, °) for (II).

Am1—O1	1.749 (4)	Am1—O21	2.461 (4)
Am1—O2	1.740 (4)	Am1—O22	2.451 (4)
Am1—O11	2.421 (4)	Am1—O31	2.464 (4)
Am1—O12	2.488 (4)	Am1—O32	2.483 (3)
O1—Am1—O2	178.85 (18)	O11—Am1—O32	66.94 (12)
O11—Am1—O12	53.09 (12)	O22—Am1—O31	66.72 (12)
O21—Am1—O22	52.93 (12)	O21—Am1—O12	68.81 (13)
O31—Am1—O32	52.55 (12)		

Data collection

Bruker Kappa APEXII area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.640, T_{\max} = 0.810$
15606 measured reflections
1167 independent reflections
1017 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.135$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.056$
 $S = 1.03$
1167 reflections
50 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.97 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.86 \text{ e } \text{Å}^{-3}$
Absolute structure: Flack (1983),
502 Friedel pairs
Flack parameter: $-0.02 (4)$

Compound (II)

Crystal data

$(\text{CH}_6\text{N}_3)[\text{Am}(\text{C}_4\text{H}_5\text{O}_2)_3\text{O}_2]$
 $M_r = 590.33$
Monoclinic, $P2_1/n$
 $a = 9.5421 (3) \text{ Å}$
 $b = 13.2830 (4) \text{ Å}$
 $c = 14.2737 (4) \text{ Å}$
 $\beta = 92.927 (2)^\circ$
 $V = 1806.80 (9) \text{ Å}^3$
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 4.29 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 $0.14 \times 0.06 \times 0.02 \text{ mm}$

Data collection

Bruker Kappa APEXII area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.712, T_{\max} = 0.924$
26314 measured reflections
5218 independent reflections
3801 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.088$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.065$
 $S = 1.00$
5218 reflections
226 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.27 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -1.16 \text{ e } \text{Å}^{-3}$

The H atoms of the CH_3 group in (I) were located in a difference Fourier map and refined as an idealized group with displacement parameters constrained to $1.5U_{\text{eq}}$ of their parent atom. The orienta-

Table 3
Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots O22 ⁱ	0.88	2.19	2.922 (6)	140
N2—H2A \cdots O21	0.88	2.04	2.874 (6)	157
N2—H2B \cdots O32 ⁱⁱ	0.88	2.04	2.876 (6)	159
N3—H3A \cdots O12	0.88	2.03	2.904 (6)	171
N3—H3B \cdots O31 ⁱ	0.88	2.12	2.977 (6)	164

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

tion of this group was refined. The H atoms in (II) were placed in calculated positions with displacement parameters constrained to $1.2U_{\text{eq}}$ of their parent atoms.

The largest electron-density peak in the final difference Fourier synthesis for (I) is 0.90 Å from atom Am1 and the deepest hole is 1.72 Å from O4. The largest electron-density peak in the final difference Fourier synthesis for (II) is 0.80 Å from Am1 and the deepest hole is 0.56 Å from H34B.

For both compounds, data collection: APEX2 (Bruker, 2006); cell refinement: SAINT-Plus (Bruker, 1998); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: YF3001). Services for accessing these data are described at the back of the journal.

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