

Americyl(v) and Americyl(vi) Chloro-complexes

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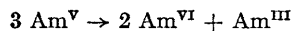
No chlorides or chloro-complexes of americium-(v) or -(vi) are known, indeed the only solid compound recorded for the latter is sodium americyl(vi) acetate. We have now found that when ethanol is added to a solution of americium(v) and caesium chloride in about 1M-hydrochloric acid, a pale green precipitate is obtained which is isostructural with the recently reported¹ neptunium complex, $\text{Cs}_3\text{NpO}_2\text{Cl}_4$. However, repeated analysis of a number of samples of the americyl(v) complex, prepared from solutions of widely differing caesium chloride concentration, suggests that the compound is $\text{Cs}_8(\text{AmO}_2)_3\text{Cl}_{11}$ rather than $\text{Cs}_3\text{AmO}_2\text{Cl}_4$. (Found: Cs, 48.1; Am, 31.5; Cl, 17.0%. $\text{Cs}_8(\text{AmO}_2)_3\text{Cl}_{11}$ requires: Cs, 47.0; Am, 31.8; Cl, 17.2% whereas $\text{Cs}_3\text{AmO}_2\text{Cl}_4$ requires: Cs, 49.3; Am, 29.6; Cl, 17.4%.)

When treated with concentrated hydrochloric acid, the compound was converted into a dark red solid, found to be the americyl(vi) chloro-complex, $\text{Cs}_2\text{AmO}_2\text{Cl}_4$. (Found: Cs, 40.0; Am, 35.3; Cl, 21.0%. $\text{Cs}_2\text{AmO}_2\text{Cl}_4$ requires: Cs, 39.1; Am, 35.4; Cl, 20.9%.) This compound exists in two crystal forms, one of body-centred cubic symmetry ($a_0 = 15.1 \text{ \AA}$), the other of monoclinic symmetry

and isomorphous with the uranyl(vi) complex, $\text{Cs}_2\text{UO}_2\text{Cl}_4$.

The formation of the americyl(vi) compound is surprising, for the AmO_2^{2+} ion is a strong oxidising agent, comparable to the ceric ion² and one would expect it to be reduced by chloride ion in acid media; experiment showed that reduction of $\text{Cs}_2\text{AmO}_2\text{Cl}_4$ to Am^{III} occurred rapidly when the salt was dissolved in 11M-hydrochloric acid, whereas slow reduction to Am^{V} (half-time about 50 min.) occurred in 0.5 M-acid; a relatively large volume of concentrated acid was required for complete dissolution because of the low solubility of the salt in it.

The formation of the americyl(vi) salt does not appear to be the result of disproportionation,



because of the amount of americium (all as Am^{III}) found in the supernatant from the preparation was much less than the 33% required by the above equation. It may be that the oxidation takes place because the lattice stabilisation energy of the americyl(vi) chloro-complex is higher than that of

the americyl(v) compound, but no data are available on this point.

The oxidation states of the two compounds were confirmed by observation of their visible spectra in dilute perchloric, nitric, or hydrochloric acid; in the infrared spectrum, the Am=O band appears at 800 cm.^{-1} in the americyl(v) complex and at 902 cm.^{-1} in $\text{Cs}_2\text{AmO}_2\text{Cl}_4$. ^{241}Am (half-life 458 years) was used for this work, the preparations being on the 50—100 mg. scale. Solutions of americium(v) in about 1M-hydrochloric acid were

obtained by dissolving the carbonato-complex, $\text{CsAmO}_2\text{CO}_3$, or better, americium(v) hydroxide obtained by the action of ozone on americium(III) hydroxide at room temperature, in the minimum volume of 6M-hydrochloric acid. This last reaction does not go to completion, but the presence of americium(III) in the acid solution, resulting from the disproportionation of americium(IV), does not interfere at low caesium chloride concentrations.

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¹ K. W. Bagnall and J. B. Laidler, *J. Chem. Soc. (A)*, 1966, 516.

² J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements", Methuen and Co. Ltd., London, 1957, pp. 357, 371.