Hydrated Double Sulphates and Chlorides of Tervalent Uranium

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It has long been known that the reddish-green solutions of the uranium(III) ion in dilute hydrochloric or sulphuric acids become intense purple-red in concentrated hydrochloric acid.[1,2] This colour soon fades under nitrogen because of oxidation by hydrogen ion unless a reducing agent is present, and pale green uranium(IV) compounds are formed. We have converted $U_2(SO_4)_3,8H_2O$, the only previously known[3] hydrated uranium(III) salt, into the olive-green double sulphates (see Table), and these give purple-red solutions in concentrated hydrochloric acid, the colour of which persists for several hours. By keeping the solutions cold and handling them under nitrogen, the crystalline, purple compounds, $M^IUCl_4,5H_2O$(M = K, Rb, NH_4), were obtained. The sodium and caesium solutions decomposed before any uranium(III) compounds could be isolated. Uranium(IV) species absorb strongly near 6500 cm.$^{-1}$ whereas uranium(III) species do not,[3] and reflectance spectra showed that the double sulphate of potassium contained a little (*ca.* 5%) uranium(IV) impurity, but that there was no detectable impurity in the other compounds.

The preparation of $5K_2SO_4,U_2(SO_4)_3$ has recently been reported.[4] It was said to be a sulphato-complex, but no results of physical measurements were given. Although our formulation of the potassium compound is different, there is partial agreement in that this is the only sulphate with marked splittings of the i.r. absorptions of the anion, and analyses and i.r. spectra show it to contain but little water.

Like $U_2(SO_4)_3,8H_2O$,[3] the double sulphates and chlorides have effective magnetic moments (Table) which are much smaller at lower temperatures.

Compound[a,b]	μ_{eff} (B.M.)		$\theta°$
	298° K	88° K	
$(NH_4)_2SO_4,U_2(SO_4)_3,9H_2O$	3·18	2·64	95
$Na_2SO_4,U_2(SO_4)_3,4H_2O$	3·23	2·72	84
$3K_2SO_4,U_2(SO_4)_3$	3·12	2·55	100
$Rb_2SO_4,U_2(SO_4)_3,8H_2O$	3·17	2·64	95
$Cs_2SO_4,U_2(SO_4)_3,11H_2O$	3·22	2·97	84
$NH_4UCl_4,5H_2O$	3·36	2·86	68
$KUCl_4,5H_2O$	3·35	2·79	70
$RbUCl_4,5H_2O$	3·32	2·76	80

[a] Satisfactory analyses were obtained although the high molecular weights make the degree of hydration (inferred from difference) somewhat uncertain, *e.g.* data for chlorides agreed with 4·5 to $5H_2O$ and i.r. spectra showed small amounts of water to be present in $3K_2SO_4,U_2(SO_4)_3$. [b] In air the sulphates are reasonably stable, but the chlorides are deliquescent and rapidly turn green.

and have plots of reciprocal susceptibility against absolute temperature which curve below the Curie–Weiss line at low temperatures.

The double sulphates and $U_2(SO_4)_3,8H_2O$ have[3] almost identical diffuse reflectance spectra consisting of groups of sharp lines from 4000 to 20,000 cm.$^{-1}$, and much broader, more intense bands at higher frequencies. In the spectra of the chlorides the sharp bands shift very slightly, mostly to lower frequencies, but the high-frequency bands change considerably. The colour of the chlorides seems mainly due to one new intense and broad band at 18,000 cm.$^{-1}$, which obscures the sharp bands in this region, and their diffuse reflectance spectra are similar to that of the uranium(III) ion in concentrated hydrochloric acid.[2] The groups of sharp lines in the visible spectra of lanthanide and actinide compounds have been assigned[2] to Laporte-forbidden transitions within the *f*-shells, and the more intense, u.v. bands to Laporte-allowed $f \rightarrow d$ transitions. As found here, the latter would be expected to be more susceptible to replacement of water molecules around the uranium(III) ion by chloride ions.

The related americium(III) compounds, $CsAmCl_4$,*ca.*$4H_2O$, $CsAmCl_4$, $Cs_2NaAmCl_6$, and Cs_3AmCl_6, have been reported recently.[5] The first compound has i.r. absorptions at 235 and 197 cm.$^{-1}$ which were assigned to Am–Cl stretching vibrations. Hydrated $RbUCl_4$ absorbs at 230 and 195 cm.$^{-1}$ with a shoulder at 202 cm.$^{-1}$ and has several vibrations at lower frequencies. We have not yet been able to prepare any hexachlorides.

We thank the S.R.C. for financial assistance.

(*Received, June 10th*, 1968; *Com.* 749.)

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