

Preparation and Properties of Hydrated Uranium(III) Sulphate

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THE chemistry of the lanthanides is dominated by the +3 oxidation state, but higher oxidation states are much more important with the actinides. Comparisons between the two series in the +3 oxidation state cannot readily be made because of

lack of experimental data. In this oxidation state, the lighter actinides are very susceptible to oxidation by air or water, and the heavier actinides are highly radioactive and not generally available. Little is known of uranium(III) compounds:

uranium(III) hydride and halides¹ have been prepared in the dry way, and visible and ultra-violet spectra of aqueous solutions of uranium(III) in perchloric acid^{2,3} and hydrochloric acid⁴ have been recorded. We report the isolation of the first hydrated uranium(III) salt, $U_2(SO_4)_3 \cdot 8H_2O$. It was crystallised by the addition of ethanol under nitrogen to the dark reddish-green solution obtained by electrolytic reduction of uranyl sulphate in dilute sulphuric acid at a mercury cathode. The solid is olive-green and very soluble in water with which it reacts rapidly to give a less-soluble, pale green uranium(IV) sulphate. The reduced solution in the electrolytic cell slowly evolves gas, but by rapid manipulation the compound can be isolated before appreciable oxidation occurs. Analysis showed the SO_4/U ratio to be 1.5, the uranium(III) and total uranium contents to be equal, and indicated an octahydrate. The dry compound is moderately stable to dry air. It is very soluble in dilute sulphuric or hydrochloric acids to give characteristic dark reddish-green

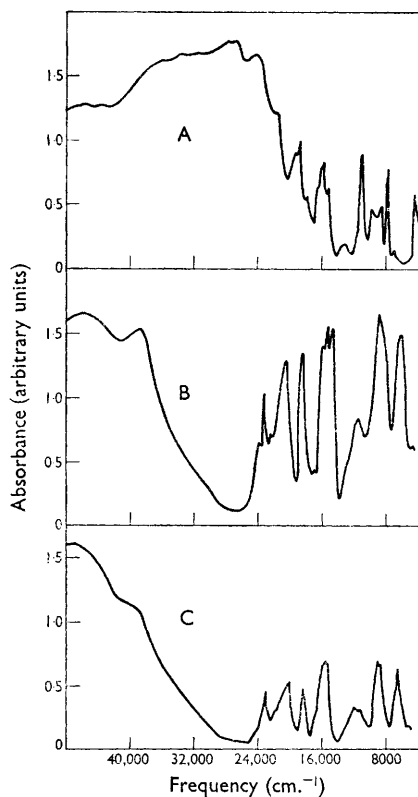


FIGURE 1. Diffuse reflectance spectra: Curve A, $U_2(SO_4)_3 \cdot 8H_2O$; Curve B, $U(SO_4)_2 \cdot 8H_2O$; Curve C, $U(SO_4)_2 \cdot 4H_2O$.

solutions which slowly decompose even under nitrogen and are rapidly oxidised by air.

Uranium(IV) tetra- and octa-hydrates have also been prepared. Reflectance spectra (Figure 1) confirm that little if any oxidation of the uranium(III) sulphate had occurred during preparation. The spectrum of the aqueous uranium(III) ion in dilute perchloric^{2,3} and sulphuric⁵ acids and the reflectance spectrum of uranium(III) sulphate are very similar.

The results of magnetic investigations of these uranium-(III) and -(IV) sulphates are shown in Figure 2. The values obtained for $U(SO_4)_2 \cdot 4H_2O$ are close to those previously reported for $U(SO_4)_2 \cdot 3 \cdot 26H_2O$.⁶ The magnetic moment of the

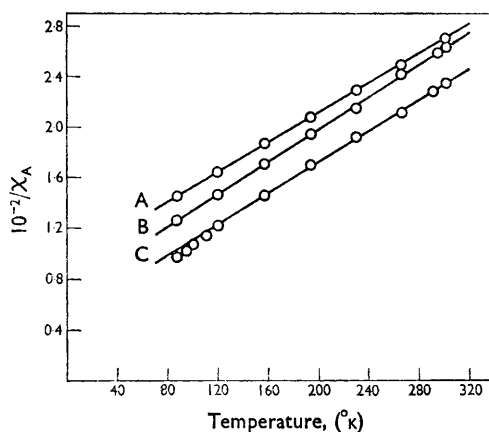


FIGURE 2. Variation with temperature of reciprocal susceptibility: A, $U(SO_4)_3 \cdot 8H_2O$; B, $U(SO_4)_2 \cdot 4H_2O$; C, $U_2(SO_4)_3 \cdot 8H_2O$.

free uranium(III) ion, ($5f^3$), is expected to be 3.62 B.M. independent of temperature.⁷ The magnetic moment of uranium(III) sulphate is less than the free-ion value and varies with temperature, ($\mu_{\text{eff}} = 3.22$ B.M. at $302^\circ K$ and 2.67 B.M. at $87^\circ K$). Extrapolation of the upper part of the χ_A^{-1} against T plot gives a Curie-Weiss constant, $\theta \approx 80^\circ$. At temperatures below about $120^\circ K$, the plot curves below the Curie-Weiss line. The aqueous uranium(III) ion has been found⁸ to have a magnetic moment of 3.17 B.M. at $293^\circ K$. Since the magnetic moments of the solid and the solution are so similar, the reduced moment of the solid is unlikely to be due to intermolecular antiferromagnetism, but to ligand field effects. The halides, UCl_3 ⁷ and UF_3 ,⁹ have similar magnetic properties to the sulphate, and the former still

has a reduced, temperature-dependent moment in dilute solid solution in LaCl_3 .

Sparingly soluble double sulphates of uranium(III) analogous to those of the lighter lanthanides have also been prepared.

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