510. *Magnetochemistry of the Heaviest Elements. Part VII.** *Sodium Plutonyl Acetate.*

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The magnetic susceptibility of sodium plutonyl acetate, measured over the temperature range 90—300° K, follows the Curie law exactly and agrees with the theoretical spin-only value for two unpaired electrons. This is taken as evidence that the ground state of the plutonyl ion has a $6d^2$ electron configuration.

Results obtained by dilution in solid solution in the diamagnetic isomorphous thorium compounds have shown that uranium and plutonium tetrafluorides have susceptibilities at infinite dilution corresponding to two and four unpaired electrons in the $6d$ and $5f$ energy levels respectively (*J.*, 1951, 2889; 1952, 1185, 1882). The dioxides have approximately the same susceptibilities at infinite dilution as the fluorides but their behaviour with increasing concentration is more complex. It was of interest to examine the sexivalent plutonium ion, which should have two unpaired electrons, and to determine whether these are in the $5f$ or the $6d$ level. The most readily characterised compound is sodium plutonyl acetate which should be magnetically dilute and has been shown to crystallise in a fluorite-type lattice ($a = 10{\cdot}64$ Å) isomorphous with sodium uranyl acetate (Zachariasen, "The Transuranium Elements," National Nuclear Energy Series, 1949, **14**, *B*, paper 20.7). No

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* Part VI, *J.*, 1952, 1882.

previous measurements have been reported on solid plutonyl compounds but the magnetic moment of Pu(VI) in solution in 0·5M-hydrochloric acid has been given as 2·91 Bohr magnetons (Calvin, Kasha, and Sheline, *ibid.*, paper 4.23).

EXPERIMENTAL

Aliquots of a pure solution of plutonium tetranitrate in dilute nitric acid were oxidised with freshly prepared silver peroxide. The plutonium was precipitated with ammonia; the precipitate was washed once with a small amount of water and was dissolved in dilute acetic acid. To this solution was added an excess of sodium acetate in dilute acetic acid, and the resulting sodium plutonyl acetate was centrifuged, washed several times with absolute ethanol, and dried in a high vacuum. The solubility of sodium plutonyl acetate in aqueous systems is quite high and so it is very difficult to free it from excess of sodium acetate. Spectrographic analyses showed that the amounts of foreign elements present as impurity were negligible.

Plutonium was determined by weighing samples of about 100 μg. on a quartz torsion fibre microbalance, dissolving the samples in known amounts of dilute nitric acid, and counting aliquots of the resulting solution on platinum discs in a methane proportional counter. The results obtained for two preparations were: A, Pu 48·2%; B, Pu 49·4% [Calc. for $NaPuO_2(C_2H_3O_2)_3$: Pu, 50·7%]. Duplicate analyses agreed within about ±0·2% and these results were interpreted as follows: Preparation A: $NaPuO_2(C_2H_3O_2)_3$, 95·0%; $Na(C_2H_3O_2),3H_2O$, 5·0%. Preparation B: $NaPuO_2(C_2H_3O_2)_3$, 97·3%; $Na(C_2H_3O_2),3H_2O$, 2·7%.

The magnetic measurements were made on a susceptibility balance described previously (Dawson and Lister, *J.*, 1950, 2177), with 1—3-mg. samples which were enclosed in Pyrex capillary tubes. After the measurements each sample tube was broken at a pre-formed scratch, and the contents were washed out. The two halves of the tube were then fused together again and the magnetic effect on the empty tube was measured. The measurements were referred to ferrous ammonium sulphate which was assumed to have a susceptibility of $32·31 \times 10^{-6}$ per g. at 20°.

The following diamagnetic corrections were applied for the calculation of the paramagnetic susceptibility of the plutonyl ion: Na^+, 3·7; $(C_2H_3O_2)^-$, 28·7; O^{2-}, 11·25; Pu(VI), 32·2; $3H_2O$, 38·9 (all $\times 10^{-6}$); the value for the acetate ion was calculated from Pascal's data (quoted by Selwood, " Magnetochemistry," Interscience Publ., 1943, Chap. III), and the others by Angus's method (*Proc. Roy. Soc.*, 1932, *A*, **136**, 569), and that for Pu(VI) was based on a $6d^2$ configuration. The results on two separate preparations are shown in the table, together with the theoretical values predicted by Hund's method (Hund, *Z. Physik*, 1925, **33**, 855).

Magnetic susceptibility of sodium plutonyl acetate.[1]

Sample		Time after pptn.	Temp. (K)	$\chi_{g.} \times 10^6$	$\chi_{m.} \times 10^6$	$\chi_{PuO_2^{++}} \times 10^6$	μ (eff.)
Sample.	*Preparation A.*						
(i)		~1 day	300	6·53	3,076	3,221	—
(ii)		~2 days	300	6·37	2,997	3,142	—
		—	200	9·94	4,680	4,825	—
		—	90	22·45	10,810	10,955	—
		—	333	5·76	2,715	2,860	—
Sample.	*Preparation B.*						
(i)		4 hrs.	300	6·62	3,119	3,264	2·80
(ii)		5 hrs.	300	6·79	3,200	3,345	2·83
		6 hrs.	200	10·73	5,056	5,201	2·88
		7 hrs.	90	23·35	11,000	11,145	2·83
		24 hrs.	300	6·69	3,152	3,297	—
		48 hrs.	300	6·64	3,126	3,271	—
		72 hrs.	300	6·60	3,110	3,255	—
		6 days	300	6·36	2,995	3,140	—
Theoretical spin-only		—	300	—	—	3,333	2·83
		—	200	—	—	5,000	
		—	90	—	—	11,110	
Theor., $5f^2$ configuration		—	300	—	—	5,334	3·58 [2]
L–S coupling		—	200	—	—	8,000	
		—	90	—	—	17,780	

[1] These results were obtained by using a magnetic field of 2500 gauss. At field strengths of 4200 and 6600 gauss the results on samples A (i) and B (i) did not differ by more than ±1%, indicating the absence of ferromagnetic impurities. [2] A $5f^2$ configuration in *j–j* coupling gives a theoretical magnetic moment of 3·84.

DISCUSSION

After the measurements on preparation A, it was suspected that the sample was slowly decomposing, to give a reduced susceptibility, and this was confirmed by making measurements at known time intervals on preparation B, sample (ii). This decomposition may be due to some instability of plutonium in the sexivalent state, but an alternative possibility is that decomposition may result from destructive bombardment of the acetate ions by the emitted α-particles, the plutonyl ion reverting to the quadrivalent oxide. A sample which was kept for several months no longer gave the characteristic X-ray diffraction pattern, and the colour changed gradually from pink to dark brown. In this connection it may be noted that in an attempt to prepare other types of compounds of sexivalent plutonium, *i.e.*, the plutonates, the thermal decomposition of barium plutonyl acetate was investigated : under conditions which were known to give barium uranate the plutonium compound yielded only a mixture of plutonium dioxide and barium oxide, as determined by the X-ray diffraction patterns.

Over a period of a few hours the drop in susceptibility is small and, from the mean of the results on preparation B, samples (i) and (ii), it may be taken as 3305×10^{-6} at 300° K. and at the moment of precipitation. Within experimental error, this is the same as the spin-only value of 3333×10^{-6} predicted theoretically by the equation

$$\mu = 2\sqrt{S(S + 1)} = 2{\cdot}83\sqrt{\chi T} \text{ where } S = 1$$

Similar agreement exists at 200° and at 90° K and there is no correlation with the theoretical values expected for a $5f^2$ electron configuration (see Table).

This behaviour is similar to that of the transition elements in which the $3d$ shell is in the process of being filled; Selwood, Lyon, and Ellis have recently shown, for instance, that the magnetic moments of chromic and ferric oxides in solid solution in aluminium oxide at infinite dilution are exactly equal to the spin-only values (*J. Amer. Chem. Soc.*, 1951, **73**, 2310). Sodium plutonyl acetate obeys the Curie law between 90° and 330° K, the Weiss constant being zero—an indication that it is a truly dilute compound and may be compared directly with chromic and ferric oxides at infinite dilution. Consequently the agreement with the spin-only value is taken as evidence for the electrons' being in the $6d$ energy level; in a magnetically dilute compound a $5f^2$ electron configuration would be expected to show some orbital contribution to the susceptibility owing to the shielding effect of the $6s$- and $6p$-electrons.

The susceptibility at room temperature is the same as that obtained previously for the quadrivalent uranium ion at infinite dilution in the UF_4–ThF_4 (*loc. cit.*) and the UO_2–ThO_2 lattices (Trzebiatowski and Selwood, *ibid.*, 1950, **72**, 4504), and in addition De Bruin, Klinkenberg, and Schuurmans (*Z. Physik*, 1944, **122**, 23) have given spectroscopic evidence that the ground state of the Th^{2+} ion has a $6d^2$-electron configuration. Consequently, as far as physical measurements are concerned the $6d$ appears to be considerably more stable than the $5f$ energy level in those ions of the seventh-period elements which have two unpaired electrons.

The author thanks Miss R. M. Elliott for the preparation of the sodium plutonyl acetate and the Director, A.E.R.E., for permission to publish the results.

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[*Received, March 20th*, 1952.]