Polymorphism in Uranyl Chelate Complexes. Part 1. Differential Scanning Calorimetry, Infrared Spectra, and *X*-Ray Patterns of Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)dioxo(trimethyl phosphate)uranium(VI)

By **John H. Levy** * and **A. Bruce Waugh**, Australian Atomic Energy Commission Research Establishment, Private Mail Bag, Sutherland, N.S.W. 2232, Australia

During thermal studies on the title complex the existence of three phases has been established by using differential scanning calorimetry, i.r., and *X*-ray diffraction techniques.

MANY metal complexes have been prepared and studied to determine whether their volatilities and thermal stabilities are suitable for gas-chromatographic determination of the metal.[1,2] For separation of metals in the actinoid series, the use of metal chelates involving β-diketones is well established.[1-3] Swain and Karraker[4] synthesised a number of chelate complexes of Th^{IV}, U^{IV}, Np^{IV}, and Pu^{IV} with 2,2,6,6-tetramethylheptane-3,5-dione and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione. Mixed-ligand complexes can also be used in gas chromatography: Mitchell and Banks[5] and Butts and Banks[6] studied complexes of lanthanoids with fluorinated β-diketones and organophosphorus adducts; and Sieck *et al.*[7] determined $[UO_2]^{2+}$ and Th^{IV} using 1,1,1,5,5,5-hexafluoropentane-2,4-dione (Hhfpd) and the neutral donor, di-n-butyl sulphoxide.

Whilst investigating a similar mixed-ligand complex, bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)dioxo(trimethyl phosphate)uranium(VI), $[UO_2(hfpd)_2\{PO(OMe)_3\}]$, with regard to its suitability for similar studies, we noted that colour changes occurred when the sample was heated to its melting point. *X*-Ray powder photographs of the sample after melting and cooling showed patterns different from those of the original material, although only slight variations in the i.r. spectra of the samples were observed. These observations seem to indicate that the complex did not decompose on heating, but that polymerisation or polymorphism occurred. In order to investigate the thermal effect on the complex in more detail, the following study was initiated.

EXPERIMENTAL

Small samples † of $[UO_2(hfpd)_2\{PO(OMe)_3\}]$ (5—20 mg) were crimped into aluminium cups to prevent volatilisation during subsequent scanning. The samples were scanned over various temperature ranges from 27 to 427 °C on a Perkin-Elmer DSC 1 differential scanning calorimeter. Infrared spectra of the samples before and after the d.s.c. experiments were recorded on a Perkin-Elmer 257 spectrophotometer. *X*-Ray powder photographs of samples were obtained with the Guinier technique using Philips–Nonius *X*-ray equipment and Cu-K_α radiation.

RESULTS AND DISCUSSION

The initial d.s.c. scan, covering the range 27—427 °C, indicated three transitions. A large exothermic peak occurs at 295 °C which represents thermal decomposition of the complex. A small endothermic peak at 88 °C is due to sample melting, whilst a smaller peak at 67 °C is attributed to a disorder transition.

In order to investigate the peak at 67 °C in more detail two further scans were made in this region. A sample was heated to just above the transition at 67 °C then cooled and rescanned. Another sample was heated to just above the m.p., then crystallised, and rescanned also. When both these samples were rescanned to the m.p. no peak at 67 °C was observed. The absence of this peak indicates a disorder within the original sample which can be annealed out. There is no observable change in either the i.r. or *X*-ray powder patterns when the original material is compared with that of a sample annealed at 70—80 °C. However, Weissenberg *X*-ray photographs of crystals of the unannealed sample showed a streaky pattern whereas annealed samples exhibited sharp spots. The occurrence of disorder in a similar type of uranyl complex {aquabis(pentane-2,4-dionato)dioxouranium(VI), $[UO_2(OH_2)(pd)_2]$} has been observed, and is indicated by streaky Weissenberg photos.[8]

After d.s.c. scans just over the m.p. at 88 °C it was noted that the freezing behaviour of the melt varied considerably, often resulting in a supercooled liquid at room temperature which did not crystallise for several days. *X*-Ray powder photographs of these samples when crystallised showed marked differences from those of the original complex. Some samples contained the original plus a new structure, whilst others contained only the new structure [Table (*b*)]. Sublimation of this new complex to a cold finger resulted in reversion to the original form. Infrared examination [Figure (*b*)] of the new complex indicated that it was very similar to the original. All the functional groups were still present and bound in the same way as in the original, indicating that decomposition had not occurred and that the new complex was probably a polymer or polymorph of the original. For convenience, the new form is designated

---

† Supplied by L. Szego of this Research Establishment.

[1] R. W. Moshier and R. E. Sievers, ' Gas Chromatography of Metal Chelates,' Pergamon, New York, 1965.

[2] C. Kutal, *J. Chem. Educ.*, 1975, **52**, 319.

[3] E. W. Berg and J. J. C. Acosta, *Analyt. Chim. Acta*, 1968, **40**, 101.

[4] H. A. Swain and D. G. Karraker, *Inorg. Chem.*, 1970, **9**, 1766.

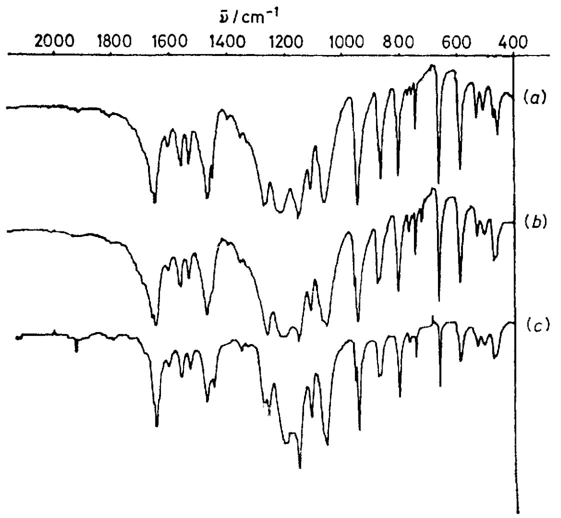
[5] J. W. Mitchell and C. V. Banks, *Analyt. Chim. Acta*, 1971, **57**, 415.

[6] W. C. Butts and C. V. Banks, *Analyt. Chem.*, 1970, **42**, 133.

[7] R. F. Sieck, J. J. Richards, K. Iversen, and C. V. Banks, *Analyt. Chem.*, 1971, **43**, 913.

[8] A. E. Comyns, B. M. Gatehouse, and E. Wait, *J. Chem. Soc.*, 1958, 4655.

β and the original α. Samples of the β form were scanned by d.s.c. and a m.p. of 88 °C was observed.



Infrared spectra of (*a*), α-, (*b*) β-, and (*c*) γ-$[UO_2(hfpd)_2\{PO(OMe)_3\}]$

X-Ray diffraction data (Å) for the α(*a*), β(*b*), and γ(*c*) forms of $[UO_2(hfpd)_2\{PO(OMe)_3\}]$. Line intensities were estimated visually

	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
(*a*)	10.80	50	4.84	40	3.52	10	2.91	5
	10.34	10	4.71	60	3.45	5	2.88	30
	9.33	100	4.51	30	3.40	30	2.79	20
	7.47	2	4.20	40	3.31	30	2.76	25
	5.91	10	3.99	30	3.26	5	2.70	10
	5.56	20	3.87	50	3.22	5	2.65	10
	5.38	15	3.79	50	3.14	2	2.61	20
	5.17	10	3.73	50	3.11	2	2.59	10
	5.03	15	3.66	5	3.06	5	2.57	10
	4.94	30	3.60	5	3.02	10		
(*b*)	10.49	100	4.66	10	3.60	40	2.88	20
	9.02	60	4.56	40	3.54	5	2.86	5
	6.15	5	4.47	15	3.52	5	2.80	5
	5.99	5	4.34	30	3.50	5	2.79	2
	5.77	60	4.05	25	3.43	2	2.74	20
	5.75	20	3.99	30	3.39	5	2.69	5
	5.66	5	3.93	30	3.28	10	2.66	5
	5.42	2	3.88	30	3.24	2	2.63	10
	5.29	50	3.87	10	3.22	5	2.61	5
	4.97	40	3.78	20	3.21	10	2.59	2
	4.90	10	3.75	20	3.00	30	2.57	2
	4.82	10	3.70	10	2.92	20	2.53	10
	4.74	10	3.63	10	2.89	5	2.52	10
(*c*) *	11.41		9.61		4.77		3.35	
	11.03		5.66		3.77		2.93	
	9.98							

* These lines were observed in addition to those of the α form in a Guinier *X*-ray photograph of a 1 : 6 mixture of γ to α. Intensities are not given as the lines were not homogeneous due to particle-size effects.

In subsequent d.s.c. scans to higher than the m.p. of the original material, followed by fast crystallisation (or crystallisation initiated with a spatula point) then rescanning, three situations arose: (*i*) the original m.p. at 88 °C was retained; or (*ii*) a new m.p. at 78 °C appeared; or (*iii*) m.p. peaks at both 88 and 78 °C of varying intensity occurred. With further crystallising and rescanning of the above three types of sample the two melting points (78 and 88 °C) continued to appear with varying intensities from 0 to 100%, indicating that a reversible transformation was taking place and that another form of the complex, γ, was formed.

The γ form was difficult to isolate because it was pressure-sensitive. This was demonstrated by dividing a mixture of the α and γ forms into two samples, one of which was ground in a mortar. Subsequent d.s.c. (in uncrimped cups) and *X*-ray analysis of the two samples revealed the disappearance of γ from the ground material, concurrent with an increase in α. Because of the difficulty of isolating the γ form, samples for i.r. and *X*-ray analysis could not be obtained using conventional grinding and mulling techniques, so the *X*-ray pattern [Table (*c*)] was obtained from a mixture of α and γ forms and the i.r. pattern was obtained by allowing a melt to self-crystallise between CsI plates [Figure (*c*)]. Again, the *X*-ray pattern indicated differences between γ, and α and β. The i.r. pattern also shows how similar the three forms are, even though slight but significant differences occur.

Because the transformations among the three forms are reversible, no major chemical changes such as decomposition or disproportionation could have been occurring. Structural isomerism as observed in pentane-2,4-dionato-complexes of platinum [9] does not occur for $[UO_2(hfpd)_2\{PO(OMe)_3\}]$ as indicated by the i.r. spectra. Polymorphism has been found in similar uranyl complexes [9] such as $[UO_2(OH_2)(pd)_2]$. For $[UO_2(hfpd)_2\{PO(OMe)_3\}]$, the evidence is consistent with the occurrence of polymorphism. Only slight differences are observed in the i.r. spectra of the three forms. Small differences such as these have been observed [10] in polymorphic glycines. The *X*-ray powder patterns are different for each form, indicating the different crystal habits. However, polymerisation in this complex cannot be discounted, for there is some suggestion that this occurs in other uranyl complexes.[8] Conclusive proof of polymorphism may be obtained by crystallographic structural studies of each of the forms. Such studies are in progress in these laboratories.

[6/2020 *Received*, 29*th October*, 1976]

---

[9] K. Nakamoto, ' Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970.

[10] J. Herranz and J. M. Delgado, *Spectrochim. Acta*, 1975, **31**, 1245.