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The Solid State Chemistry of Uranium.
Part 2. Structure and Thermal Reactions of $UO_2(NO_3)_2 \cdot 2tmu$

C. P. J. VAN VUUREN*

Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa

and P. H. VAN ROOYEN

National Chemical Research Laboratory, CSIR, P.O. Box 395, Pretoria, 0001, South Africa

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The thermal reactions and crystal structure of $UO_2Cl_2 \cdot 2tmu$ (tmu = tetramethylurea) were described in a previous publication [1]. It was shown that the compound decomposed to yield a stable intermediate, $UO_2Cl_2 \cdot tmu$. Raman data suggested that this intermediate can be described as a chloride-bridged dimeric compound. It was therefore of interest to obtain similar solid state data for $UO_2(NO_3)_2 \cdot 2tmu$ and to compare it with that described for $UO_2Cl_2 \cdot 2tmu$.

Experimental

The compound was prepared by mixing acetone solutions of tmu and $UO_2(NO_3)_2 \cdot 6H_2O$ which gave a clear yellow solution. Crystals suitable for X-ray diffraction, were obtained upon standing at room temperature. The structure was solved by a single crystal X-ray study.

Thermal studies were conducted on a Stanton Redcroft simultaneous TG/DTA-MS system and Du Pont 910 differential scanning calorimeter. The experimental methods used, were described previously [1, 2].

Crystal Data (22 °C)

Monoclinic, space group $P2_1/n$, $a = 8.605(3)$, $b = 12.444(4)$, $c = 10.098(3)$ Å, $\beta = 111.73(3)°$, $V = 1004(1)$ Å^3, $Z = 2$, $D_m = 2.07$ g cm^{-3}, μ = (Mo Kα) = 77.7 cm^{-1}. Mo Kα radiation (graphite monochromator) $\lambda = 0.71069$ Å, $3 \leqslant \theta \leqslant 27°$, crystal dimensions 0.32 × 0.28 × 0.20 mm was used for intensity data collection.

Final R and R_w values were 0.021 and 0.018 respectively for 1493 observed reflections $[I > 2\sigma(I)]$ of 2287 independent reflections measured on an Enraf-Nonius CAD4F diffractometer. The intensity data were corrected for Lorentz, polarization and absorption effects.

TABLE I. Fractional Coordinates (× 10^4, × 10^3 for H) and Equivalent Isotropic Thermal Parameters (× 10^3 Å^2). $U_{eq} = \frac{1}{3}\Sigma_{ij}U_{ij}a_i^*a_j^*(a_i \cdot a_j)$

	x/a	y/b	z/c	U_{eq}
U	5000	5000	5000	31(1)
O(1)	3714(4)	6129(3)	4850(4)	47(1)
O(2)	4204(5)	4852(4)	2335(4)	58(1)
N(1)	2864(7)	4332(4)	2050(6)	50(1)
O(3)	2485(5)	4111(3)	3128(4)	56(1)
O(4)	2002(6)	4074(4)	857(5)	78(1)
O(5)	3406(4)	3953(3)	5942(4)	44(1)
C(1)	2167(6)	3411(4)	5955(5)	35(1)
N(2)	1854(6)	2443(4)	5361(5)	46(1)
C(2)	3118(9)	1930(5)	4930(9)	64(2)
C(3)	164(9)	2016(6)	4663(8)	67(2)
N(3)	1221(5)	3802(4)	6624(5)	43(1)
C(4)	425(8)	3116(7)	7361(8)	64(2)
C(5)	1421(9)	4917(9)	7051(8)	69(2)
H(1)	298(8)	220(5)	399(7)	98(7)^a
H(2)	423(7)	222(5)	553(6)	98(7)^a
H(3)	291(8)	116(5)	507(7)	98(7)^a
H(4)	12(8)	185(5)	363(7)	98(7)^a
H(5)	−53(8)	258(5)	466(7)	98(7)^a
H(6)	5(8)	130(5)	528(6)	98(7)^a
H(7)	229(8)	502(6)	794(6)	98(7)^a
H(8)	148(7)	536(5)	629(6)	98(7)^a
H(9)	38(7)	519(5)	723(6)	98(7)^a
H(10)	−78(8)	320(5)	680(6)	98(7)^a
H(11)	61(8)	345(5)	823(7)	98(7)^a
H(12)	93(8)	233(5)	746(7)	98(7)^a

^{a}Isotropic temperature factor.

The structure was solved using standard methods in SHELX 76 [3] and refined using full matrix least-squares techniques. All the hydrogen atoms were located in experimental positions and were included in the refinement with a common isotropic thermal parameter that refined to U(H) = 0.098(7) Å^2. The atomic coordinates and equivalent isotropic thermal parameters are listed in Table I.

Results and Discussion

A perspective view of the molecular structure is given in Fig. 1 and selected interatomic distances and angles are listed in Table II. The uranium atom lies on a crystallographic centre of symmetry. The uranyl, U=O distances as well as the U–O (tmu) distances are similar to that observed in the chloro complex [1] suggesting similar uranyl–ligand interactions. Thermal analysis, simultaneous TG/DTA-MS, of the compound in flowing argon and a heating rate of 10 °C min^{-1}, suggests that the endothermic process, beginning at about 150 °C, consists of at least two

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*Author to whom correspondence should be addressed.

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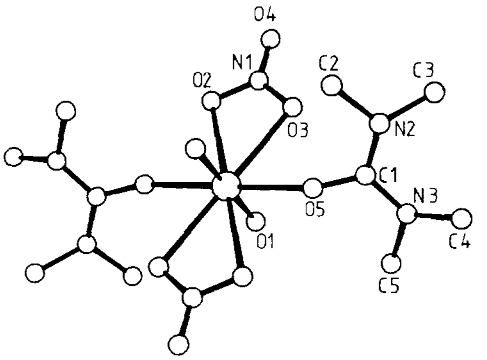

Fig. 1.The molecular structure of $UO_2(NO_3)_2 \cdot 2tmu$.

TABLE II. Selected Bond Distances (Å) and Angles (°) in $UO_2(NO_3)_2 \cdot 2tmu$

Distances			
U–O(1)	1.760(3)	U–O(2)	2.526(4)
U–O(3)	2.539(4)	U–O(5)	2.335(3)
C(1)–O(5)	1.265(5)		
Angles			
O(1)–U–O(2)	93.0(2)	O(1)–U–O(3)	87.0(1)
O(2)–U–O(3)	49.8(1)	O(2)–N(1)–O(3)	114.7(5)
O(3)–N(1)–O(4)	122.7(5)	C(1)–O(5)–U	157.8(3)

overlapping processes; melting of the compound which is followed by dissociation of the tmu at about 170 °C. This is in contrast to the chloro complex, in which case no melting was observed. This endothermic process is followed by an overlapping exothermic process leading to an ignition reaction of the type seen for many pyrotechnic materials, with an uncontrolled rise in temperature at 223 °C. This is probably due to oxidation of the tmu since evolved gas analysis indicated the presence of CO_2 and H_2O in addition to the NO_2 and NO, which can be regarded as breakdown products of the nitrate [4, 5]. The final mass loss was 54.7% and correspond to the formation of UO_3. The mass loss calculated for

$$UO_2(NO_3)_2 \cdot 2tmu(s) \longrightarrow UO_3(s) + \text{volatile products}$$

is 54.31%.

A lower rate of heating, 3 °C min^{-1}, produced a similar reaction but not as exothermic as the one observed at 10 °C min^{-1}. This could be due to the fact that the decomposition of the nitrate is much slower at this heating rate, resulting in smaller concentrations of the oxidising agents, probably NO_2 and NO, in the dynamic argon atmosphere. The DSC trace (Fig. 2) of the reaction, recorded at 3 °C min^{-1}, clearly illustrates the overlapping processes as discussed above.

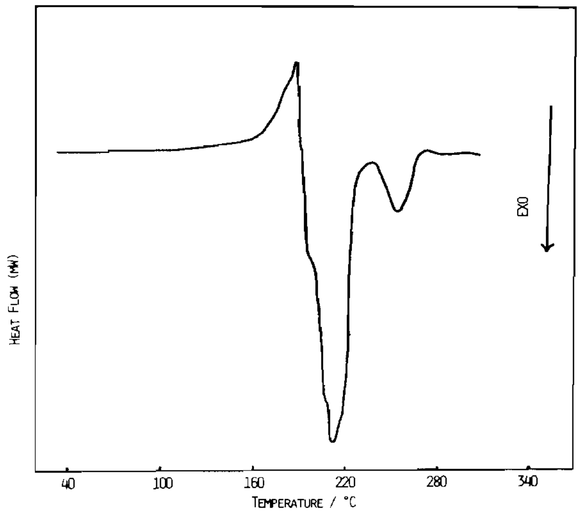

Fig. 2. DSC curve for the decomposition of $UO_2(NO_3)_2 \cdot 2tmu$. Heating rate: 3 °C/min in argon atmosphere.

Supplementary Material

Lists of structure factors, interatomic distances and angles are available on request from the authors.

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