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Thermal decomposition of ammonium dioxodiaquaperoxyoxalatouranate(VI) hydrate

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Abstract

The chemical analysis and the thermal decomposition of the complex are consistent with the formation of an intermediate, which is a mixture of ammonium carbonate and uranium trioxide, subsequently decomposing to ammonium uranate. The ammonium uranate decomposes to uranium trioxide which is finally reduced to U_3O_8. Thermal decomposition, infrared absorption spectra, and X-ray diffraction patterns are used to characterize the complex and the intermediate products of the thermal decomposition. Based on this data, the complex salt may be represented as $(NH_4)_2[UO_2(O_2)(C_2O_4)(H_2O)_2]\cdot H_2O$.

Keywords: Thermal analysis; Uranium(VI); Ammonium salt; X-ray diffraction

1. Introduction

It has been shown spectrophotometrically that peroxyoxalatouranate anion is formed when hydrogen peroxide is added to a solution of uranyl oxalate [1].

The change in pH in the titration of a solution of uranyl perchlorate, hydrogen peroxide and sodium oxalate with sodium hydroxide affords further evidence for the formation of this ion in solution [2]. A solid of composition $(NH_4)_2[U_2O_4(O_2)(C_2O_4)_2]$ was precipitated on the addition of hydrogen peroxide to a saturated solution of ammonium uranyl oxalate (or a concentrated solution of ammonium and uranyl oxalates in appropriate amounts) [2,3]. The analysis though not exact supports the proposed formula quite closely.

In the presence of excess oxalate ion the formation of a peroxydioxalatouranate(VI) species was also detected spectrophotometrically [1]. By adding hydrogen peroxide to a solution saturated in both uranyl and ammonium oxalates, a yellow solid of composition $(NH_4)_6[U_2O_4(O_2)(C_2O_4)_4]\cdot 7H_2O$ was obtained [3]. The formula indeed represents the dimeric form of the peroxydioxalatouranate(VI) complex. When hydrogen peroxide was added to a solution containing less ammonium oxalate no precipitate was formed, but alcohol precipitated a different hydrate of the same anion $(NH_4)_6[U_2O_4(O_2)(C_2O_4)_4]\cdot 3H_2O$ [3].

A third ammonium peroxyoxalatouranate(VI), formulated as $(NH_4)[UO_2(O_2)C_2O_4]\cdot nH_2O$, has been obtained by adding 30% hydrogen peroxide to a 14% solution of ammonium uranyl oxalate [1] while a fourth, described as $(NH_4)_2[U_2O_4(O_2)_2C_2O_4]\cdot nH_2O$ has been mentioned in another report [2]. It is not clear whether the last two compounds are really different [1].

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In the present work, the ammonium dioxodiaquaperoxyoxalatouranate(VI) complex was prepared by the reaction of UO_2^{2+} with oxalic acid and then hydrogen peroxide in the presence of ammonium ion. The thermal decomposition of the complex has been studied and a detailed account of the mechanism has been worked out on the basis of the thermal data, infrared spectroscopic and X-ray diffraction studies.

2. Experimental

2.1. Instrumentation

2.1.1. Thermal analysis unit

SEIKO combined thermal analysis system (TG/DTA-32), temperature programmable thermal balance and platinum crucible as container is used for measuring the thermograms in air. The rate of heating was fixed to 10 °C/min and the sensitivity of the instrument to 0.1 mg.

2.1.2. Infrared spectroscopy

The infrared spectra of the complexes were recorded on a SHIMADZU FTIR-8201 PC Infrared Spectrophotometer in KBr pellets.

2.1.3. X-ray diffraction data

An X-ray diffractometer of Rich Seifert & Co. attached to a microprocessor was used to measure the X-ray diffraction patterns using Cu Kα1 ($\lambda = 1.540598$ Å).

2.2. Preparation and analysis

The ammonium dioxodiaquaperoxyoxalatouranate(VI) complex salt was prepared by using the following procedure [4].

About 1.0 g (1.99 mmol) sample of $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in water (10–15 cm^3) followed by addition of 25% ammonium hydroxide solution with stirring, until a yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of ammonium and nitrate ions. To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of a concentrated solution of oxalic acid to obtain a clear solution, which was stirred for ca. 5 min. A 25 cm^3 (220.5 mmol) sample of 30% H_2O_2 was added, while the $U:C_2O_4:H_2O_2$ ratio was maintained at 1:1:111 and the solution was stirred for ca. 15 min followed by the careful addition of the ammonium hydroxide solution until the pH was raised to 6, where upon a yellow product just began to appear. An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline complex of ammonium dioxodiaquaperoxyoxalatouranate(VI) hydrate. The compound was allowed to settle for ca. 20 min, separated by centrifugation, purified by washing with ethanol (3–5 times) and finally dried in vacuo over silica gel. The compound obtained was tested to confirm the absence of nitrate.

The reaction of hydrogen peroxide with uranyl ion leading to a complex peroxyuranate(VI) of definite composition is highly dependent on the pH of the reaction medium. Thus, evaluation of an appropriate pH for successful synthesis of a peroxyuranate species was an important prerequisite. A suitable pH for bringing about the coordination of both peroxide and oxalate with the uranyl center was ascertained to be 6. The compounds isolated at a relatively lower pH (e.g. ca. 4) on being analyzed did not show any peroxide to the desired level (i.e. $U:O_2^{2-}$ as 1:1), indicating therefore that the O_2^{2-} uptake process was in progress but did not reach the $U:O_2^{2-}$ ratio of 1:1.

The compound was analyzed for its uranium(VI), oxalate, peroxide and water content. Uranium(VI) was

Table 1
Chemical analysis data of ammonium dioxodiaquaperoxyoxalatouranate(VI)

Composition (%)					Mole ratio	Possible formula
U(VI)	$C_2O_4^{2-}$	O_2^{2-}	NH_4^{+}[a]	H_2O[a]	$U(VI):C_2O_4^{2-}:O_2^{2-}$	
53.37	19.54	7.22	7.95	11.92	1:1:1	$(NH_4)_2[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O$

[a] Calculated from the formula.

estimated by the photochemical reduction with alcohol [5] and oxalate and peroxide by volumetric titration with standardised cerium(IV) sulpahate [6,7]. The water content was determined by the difference and from the thermal data. The results of the analyses are shown in Table 1.

3. Results and discussion

3.1. Thermal studies

3.1.1. Thermogravimetric analysis (TGA)

The thermogram of ammonium dioxodiaquaperoxyoxalatouranate(VI) hydrate and the data obtained from it are given in Fig. 1. The TG curve shows that the loss of water took place in two steps. The first was the removal of crystal water of crystallization which corresponds to a weight loss of 3.31% (at 59.3 °C) compared to the calculated value of 3.75%. The second was due to the loss of the two molecules of coordinated water corresponding to 12.67% (at 97.3 °C) of the total weight loss (ca. 11.25%).

The steepness of the weight loss curve between 97.3 and 232 °C indicated a significant weight loss which may be attributed to the formation of a carbonate intermediate.

The anhydrous intermediate product, which is possibly ammonium dioxoperoxyoxalatouranate(VI) $(NH_4)_2[UO_2(O_2)C_2O_4]$ was assumed to be thermally unstable and hence underwent decomposition at the above temperature range to give $(NH_4)_2CO_3{\cdot}UO_3$ [5]. This intermediate was possibly a mixture of ammonium carbonate and uranium trioxide, the later being unstable under the condition, may decompose to ammonium uranate [8]. The ammonium uranate

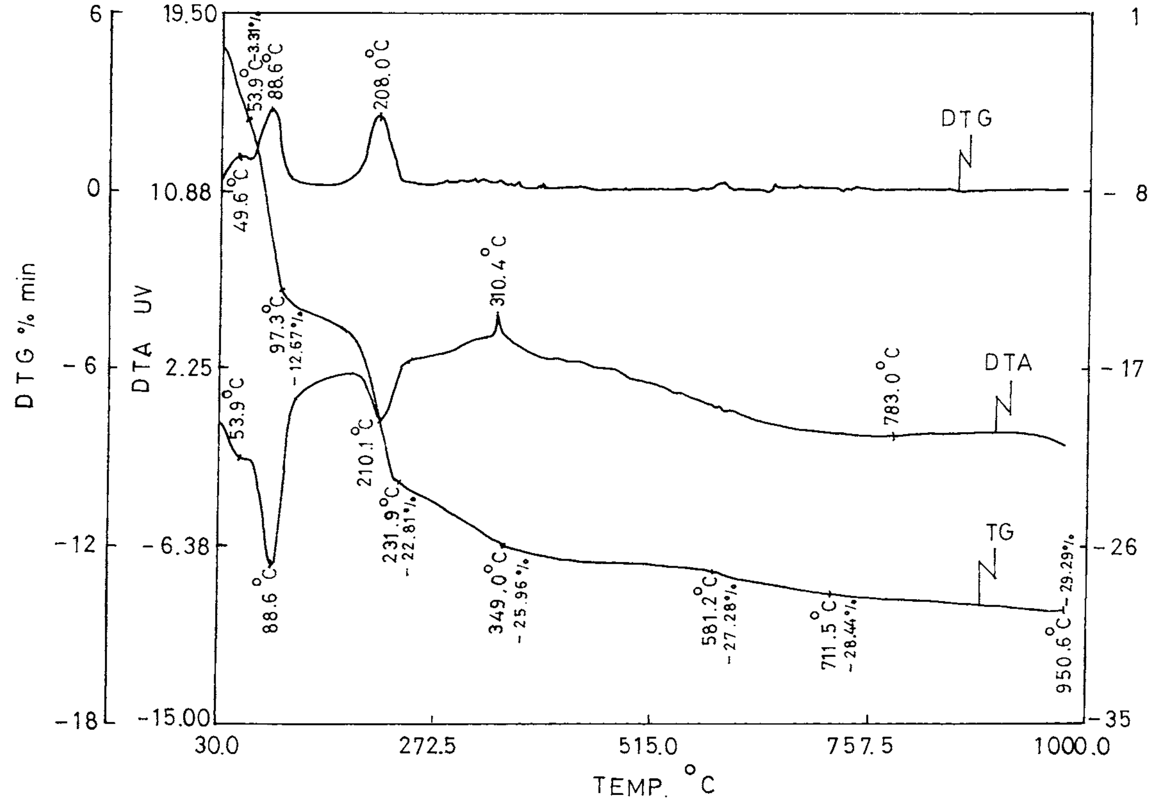

Fig. 1. TG/DTA curve of ammonium dioxodiaquaperoxyoxalatouranate(VI) hydrate.

decomposes to oxides of uranium with variable composition. The observed oxide is probably UO_3 which further reduces to U_3O_8 as reported earlier [9,10].

3.1.2. *Differential thermogravimetric analysis (DTG)*

The DTG curve of ammonium dioxodiaquaperoxyoxalatouranate(VI) is also shown in Fig. 1. From the figure it is evident that there are two adjacent peaks corresponding to a two-step dehydration of the complex. The first peak having $\Delta T_{\max}$ at 88.6 °C and a shoulder at about 49.6 °C indicates the formation of the anhydrous product. The second significant loss at 208 °C is attributed to the decomposition of the later to $(NH_4)_2CO_3 \cdot UO_3$.

3.1.3. *Differential thermal analysis (DTA)*

The DTA results of the compound are also shown in Fig. 1. From the DTA curve it is evident that the endotherm with $\Delta T_{\min}$ at 88.6 °C and a shoulder at 53.9 °C indicates a two-step dehydration of the complex. The DTA thermal responses correspond to the loss of the crystal and coordinated water, respectively. There is also an endotherm at 210.1 °C corresponding to the formation of an unstable intermediate product, which was possibly a mixture of ammonium carbonate and uranium trioxide. An exotherm with a sharp peak and $\Delta T_{\max}$ at 310.4 °C indicates the detachment of ammonia from ammonium uranate [10].

3.2. *Infrared spectra of ammonium dioxodiaquaperoxyoxalatouranate(VI)*

The IR spectra of ammonium dioxodiaquaperoxyoxalatouranate(VI) hydrate and the products obtained by heating the complexes at 90 and 250 °C and cooled to the room temperature are given in Fig. 2(A)–(C) and Table 2 respectively. From the spectra of the original complex it is noted that the distinctly strong and sharp bands at 907, 723 and 606 cm^{-1} have been assigned to the ν(U=O) (trans-linked O=U=O) [11], ν(O–O) (the peroxy modes) [12–21], and $\nu(U{-}O_2)$ respectively. The peak at 606 cm^{-1} also indicates the presence of crystal water [22]. The definite presence, shapes and positions of ν(O–O) and the complementary $\nu(U{-}O_2)$ modes in the regions stipulated by the presence of triangularly bonded bidentate peroxide led to the inference that the $O_2{}^{2-}$ group is bonded to the $UO_2{}^{2+}$ center in a triangular bidentate (C_{2v}) manner. The IR modes due to the coordinated $C_2O_4{}^{2-}$ ligand (at 1634 cm^{-1}) are quite straight forward and unequivocal show the presence of a chelated oxalato group [22–25]. The ν(O–H) and δ(H–O–H) bands in the IR spectra of the compounds resemble in their shapes and positions those generally observed for the coordinated water [26,27]. Nevertheless, results as well as the loss of water as evident from the pyrolysis studies suggest that the water molecules in the complex occur both as lattice and coordinated water.

A very strong absorption at 3499 cm^{-1} corresponds to the stretching mode of [28]. Similarly, a very broad and very strong absorption at 1634 cm^{-1} may be due to the bending vibrations of H–O–H [29] and asymmetric stretching vibrations of C=O [18–20]. Moreover, the presence of a very broad and strong absorption at 3171 cm^{-1} is assigned to the stretching mode of vibration of N–H indicating the presence of ammonium ion [30].

There is a similarity in the spectra of the original complex and the first decomposition product suggesting that the water only is removed from the former. The difference in the shape of the bands at around 3500 and 1600 cm^{-1} regions clearly indicates this. On the other hand, the spectrum of the second decomposition product shows that some of the characteristic bands of the original complex and the first decomposition product are missing. Particularly lack of significant peaks in the lower frequency region (~600 cm^{-1}), which are supposed to be due to the stretching modes of vibrations of the –O–O– and the $U{-}O_2$ linkages is suggesting that the original complex has undergone step-wise decompositions. However, the band assigned to the ν(U=O) appears to be more intense in both the decomposition products as compared to the original complex indicating the possible transformations of the uranium–oxygen linkage. The broad bands in the range of 3500–3000 cm^{-1} for the decomposition products may be due to the absorption of moisture from the atmospheric air combined with the N–H stretching modes of vibrations.

3.3. *X-ray diffraction data*

The X-ray diffraction data of ammonium dioxodiaquaperoxyoxalatouranate(VI) and that of the product

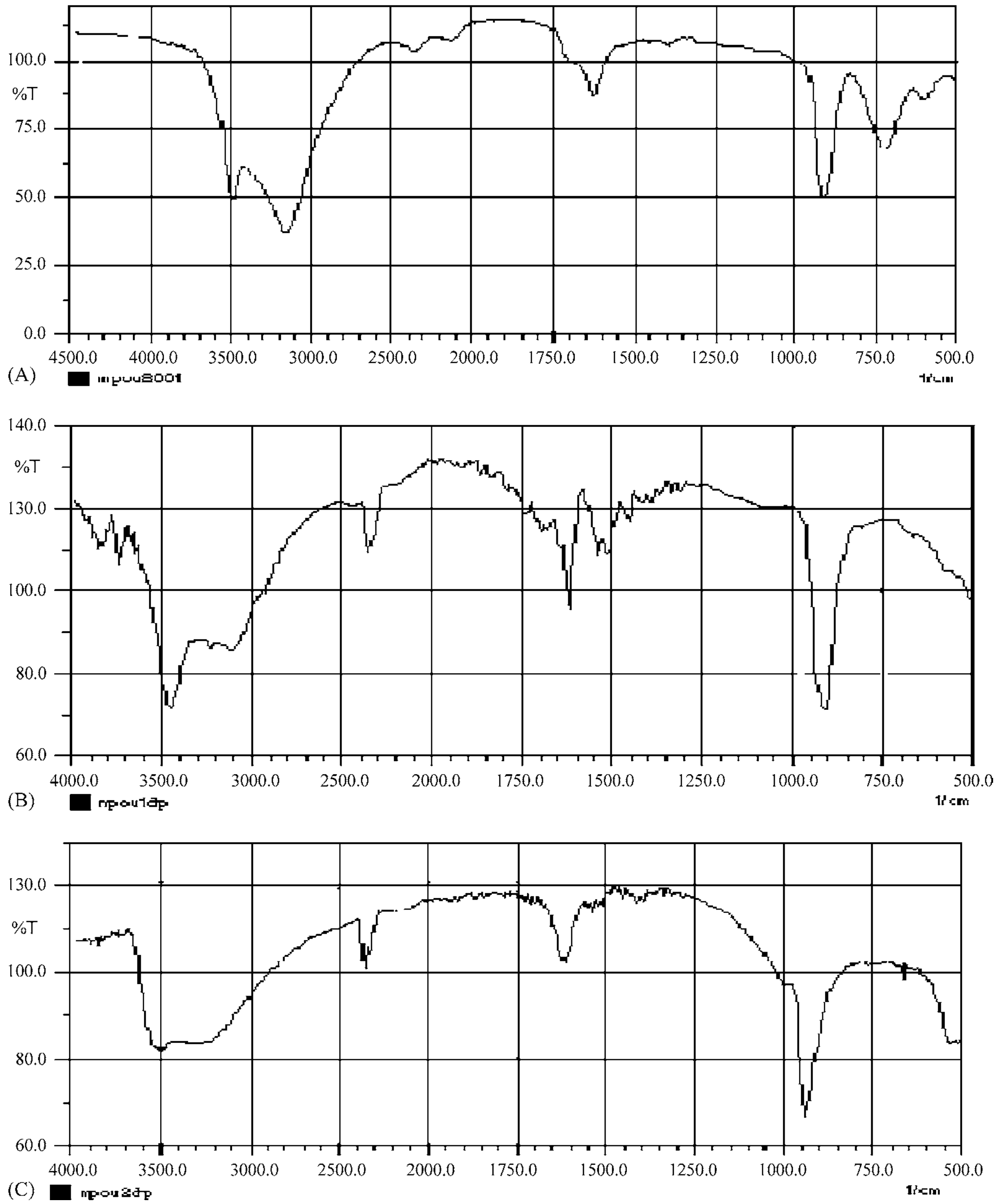

Fig. 2. (A) Infrared spectrum of ammonium dioxodiaquaperoxyoxalatouranate(VI) hydrate; (B) infrared spectrum of ammonium dioxodiaquaperoxyoxalatouranate(VI) after heating to 90 °C; (C) infrared spectrum of ammonium dioxodiaquaperoxyoxalatouranate(VI) after heating to 250 °C.

obtained after heating the original complex to 90 and 250 °C and cooling are given in Table 3 along with those of uranium(VI) oxalate and ammonium oxalate for the comparison.

The data cited in the table clearly shows that the heated product obtained at 90 °C is a single compound and not a mixture of ammonium and uranyl oxalates.

Table 2
Infrared absorption data of ammonium dioxodiaquaperoxyoxalatouranate(VI) and the decomposition products[a]

Complex			Band assignment
Original (cm^{-1})	Heated at 90 °C (cm^{-1})	Heated at 250 °C (cm^{-1})	
3499 sp	3450 sp, s		$\nu_{as,s}$(H–O–H)
	3230 b		$\nu_{as,s}$(H–O–H)
3171 b, s	3110 b	3200 vb	νN–H
1634 m	1640 sp, s		
	1535 m		ν_a(C=O) + δ(H–O–H)
	1500 m		
1437 vw	1460 w		ν_s(C=O) + δ(O–C=O)
		1650 sp, m	ν_s(C–O) may be due to CO_3^{2-}
		1350 w	ν_s(C–O) may be due to CO_3^{2-}
907 sp, s	900 sp, s	950 sp, s	ν(U=O)
723 m			ν(O–O)
606 b, w			ν(U–O_2)

[a] b: broad; m: medium; s: strong; sp: sharp; sh: shoulder; w: weak.

The complex was also heated to 250 °C and maintained at this temperature for half an hour. The product obtained in this manner was tested for the presence of carbonate by the usual acid test. The result of this test indicated the presence of carbonate in the product.

On the basis of the above thermal data, the compound was represented by the structural formula

Table 3
X-ray diffraction data of ammonium dioxodiaquaperoxyoxalatouranate(VI) and the product after heating it to 90 and 250 °C compared with uranium(VI) oxalate and ammonium oxalate monohydrate

NH_4^+ complex	Complex heated to 90 °C	Complex heated to 250 °C	$UO_2C_2O_4$	$(NH_4)_2C_2O_4 \cdot H_2O$
		6.249_x		6.320_9
5.869_x	5.0982_x	5.235_8		
4.225_1	4.2823_4	4.171_6	4.87_6	4.380_7
3.422_4	3.4748_4	3.445_6	4.57_6	
3.393_1	3.7263_4	3.310_6	4.46_x	3.256_6
2.947_1		2.825_8		2.666_x
2.488_1	2.4409_2			2.142_3
2.359_1	2.3708_2			
2.231_1	2.1654_1			2.041_1
2.015_1	2.0239_1			2.008_2
1.966_1	1.9323_2	1.866_7		1.870_6
	2.6275_2	1.749_7		1.750_2
	1.8470_1			
	3.2031_1	1.408_6		
	2.0858_1	1.357_7		
	1.9126_2			
	1.7501_1	1.594_7		1.668_2
	1.2887_1			
	1.4833_1	1.794_5		1.696_2
	1.3389_1	1.461_4		
	1.4370_1			
	2.7085_2			
	1.6338_1			
	1.5121_0			
	1.3661_0			

$(NH_4)_2[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O$. Based on the results of these investigations the following thermal decomposition mechanism is proposed:

$$\begin{aligned}&(NH_4)_2[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O\\ &\overset{30-53.9^\circ C}{\rightarrow}(NH_4)_2[UO_2(O_2)C_2O_4(H_2O)_2]\\ &\overset{53.9-97.3^\circ C}{\rightarrow}(NH_4)_2[UO_2(O_2)C_2O_4]\\ &\overset{97.3-232^\circ C}{\rightarrow}(NH_4)_2CO_3\cdot UO_3\overset{232-300^\circ C}{\rightarrow}(NH_4)_2UO_4\\ &\overset{\sim300-\sim600^\circ C}{\rightarrow}UO_3\overset{\sim650-\sim950^\circ C}{\rightarrow}U_3O_8\end{aligned}$$

and overall:

$$\begin{aligned}&(NH_4)_2[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O\\ &\rightarrow (NH_4)_2UO_4 + 3H_2O + 2CO_2\end{aligned}$$

The literature [31] suggests that uranyl ion (which has a linear structure) has conventionally been assumed to be the center of the complex, as it does not take part in the inner-sphere substitution reactions and remains unchanged. Besides, uranyl ion exhibits six coordination. Hence, it can be concluded from the results of the above investigation that the complex has an octahedral structure with composition

$$(NH_4)_2[UO_2(O_2)C_2O_4(H_2O)_2]\cdot H_2O$$

References

[1] E.V. Komarov, A.M. Ggurevich, Izv. Akad. Nauk., SSSR Otd. Khim. Nauk. (1959) 547.
[2] I.I. Chernayev, V.A. Golovnya, G.V. Ellert, Zh. Neorgan. Khim. 6 (1961) 790.
[3] A. Mazzucchelli, F. Bimbi, Atti. Accad. Nazl. Lincei. Rend. Classe Sci. Fiz. Mat. Nat. [5] 16 (III) (1907) 576.
[4] M. Bhattacharjee, M.K. Chaudhuri, R.N.D. Purkayastha, Inorg. Chem. 25 (1986) 2354.
[5] G.G. Rao, V.P. Rao, N.C. Venkatamma, Zeitschrift für analytische Chemie 150 (3) (1956) 178.
[6] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd Edition, The English Language Book Society and Longman, London, 1961, p. 320.
[7] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd Edition, The English Language Book Society and Longman, London, 1961, p. 325.
[8] N.D. Dahale, K.L. Chawla, N.C. Jayadevan, V. Venugopal, Thermochim. Acta 293 (1997) 163.
[9] T. Sato, F. Ozawa, S. Shiota, Thermochim. Acta 88 (1985) 313.
[10] A.M. Gadalla, A.F. Bishay, Z.M. Zayed, Thermochim. Acta 62 (1983) 217.
[11] K.W. Bagnal, D. Brown, J.F. Easey, J. Chem. Soc. A (1968) 22.
[12] M.K. Chaudhuri, S.K. Ghosh, Polyhedron 1 (1982) 553.
[13] M.K. Chaudhuri, S.K. Ghosh, Inorg. Chem. 21 (1982) 4020.
[14] M.K. Chaudhuri, S.K. Ghosh, Inorg. Chem. 23 (1984) 534.
[15] M.K. Chaudhuri, S.K. Ghosh, J. Chem. Soc., Dalton Trans. (1984) 507.
[16] C. Djordjevic, Chem. Br. 18 (1982) 554.
[17] C. Djordjevic, S.A. Craig, E. Sinn, Inorg. Chem. 24 (1985) 1283.
[18] W.P. Griffith, J. Chem. Soc. (1963) 5345.
[19] W.P. Griffith, J. Chem. Soc. (1964) 5248.
[20] W. Griffith, T.D. Wickins, J. Chem. Soc. A (1968) 397.
[21] M.K. Chaudhuri, B. Das, Inorg. Chem. 24 (1985) 2580.
[22] J. Fujita, A.E. Martell, K. Nakamoto, J. Chem. Phys. 36 (1962) 324, 331.
[23] N.F.J. Curtis, Chem. Soc. (1963) 4109.
[24] N.F.J. Curtis, Chem. Soc. (1964) 2644
[25] N.F.J. Curtis, J. Chem. Soc. A (1968) 1584.
[26] A.J. Edwards, J. Chem. Soc. A (1971) 2653.
[27] M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta, D.T. Khathing, J. Chem. Soc., Dalton Trans. (1981) 2587.
[28] P.J. Lucchesi, W.A. Glasson, J. Am. Chem. Soc. 78 (1956) 1347.
[29] J. Fujita, K. Nakamoto, M. Kobayashi, J. Am. Chem. Soc. 78 (1956) 3963.
[30] N.S. Gill, P.H. Nuttal, D.E. Scaife, D.W.A. Sharp, J. Inorg. Nucl. Chem. 18 (1961) 79.
[31] I.I. Chernyaev, V.A. Golovnya, G.V. Ellert, R.N. Shcholokov, V.P. Markov, The structure of complex uranyl compounds, in: Proceedings of 2nd UN International Conference on Peaceful Uses of Atomic Energy, Geneva, Acad. Sci. USSR, Moscow, 28, 1958, pp. 235–249.