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SYNTHESIS OF SOME 1-FLUOROARYL-1,3-DIKETONES, BIS(1,3-DIKETONATO)COPPER(II), BIS(1,3-DIKETONATO)DIOXOURANIUM(VI), AND THEIR ELECTROPHILIC SUBSTITUTION REACTIONS

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ABSTRACT

Some 1-fluoroaryl-1,3-diketones were prepared by treatment of methyl 1-fluoroaryl ketone with ethyl acetate, ethyl fluoroacetate or ethyl pentafluoropropionate in the presence of sodamide which were characterized in the form of their copper chelates. 1-Substituted-aryl-1,3-diketones (**1a-h**) in turn on treatment with uranyl acetate afforded corresponding

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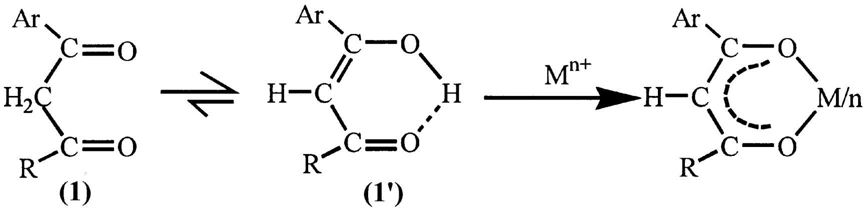
bis(1,3-diketonato) dioxouranium(VI) (**3a-f**). Bis(1,3-diketonato)dioxouranium(VI) (**3a-f**) when subjected to electrophilic bromination or nitration reactions yielded bis(2-bromo-1,3-diketonato)dioxouranium(VI) (**4a-e**) and bis(2-nitro-1,3-diketonato)dioxouranium(VI) (**5a-e**), respectively. The bonding mode of the ligands to the uranium ion has also been determined from IR and ^{1}H NMR spectral studies.

INTRODUCTION

The chemistry of 1,3-diketones has attracted the attention of scientists for almost a century[1]. Diverse applications of 1,3-diketones as intermediates for the synthesis of various biologically active heterocyclic compounds[2–6], herbicides[7], photoprotectant against skin damage[8], *etc.* have been reported in the literature from time to time during the last three decades. Sulfur-containing 1,3-diketones have also been used for the treatment of liver diseases[9]. Metal 1,3-diketonates have found application in the production of laser devices[10], as NMR shift reagents[11] and in analytical chemistry[12]. Neodymium 1,3-diketonates have found applications as shielding agents for plastics[13] and europium complexes have been used as UV-sensitive luminescent compounds for ink and resins[14].

A comprehensive account of the chemistry of metal 1,3-diketonates has been given by Mehrotra *et al.*[15] Joshi and Pathak[16] have reviewed the overall characteristics of 1,3-diketonates with emphasis on fluorinated 1,3-diketonates. Bala-Subramanian *et al.*[17] have reviewed the substitution reactions of coordinated 1,3-diketones, 1,3-diketoamines and thio-1,3-diketones.

Metal 1,3-diketonate systems behave as reactive heterocycles possessing at least some aromatic character (Fig. 1). The quasi-aromatic nature of fluorinated 1,3-diketonatochromium(III)[18] and fluorinated tris(1,3-diketonato)europium(III)[19] systems have been reported from our laboratories. However, a perusal of the literature revealed that there is only one report on the electrochemical synthesis and quasi-aromatic nature of uranyl 1,3-diketonates[20]. Therefore, as a part of our comprehensive program, the synthesis of some new 1-fluoroaryl-1,3-diketones (**1f-h**), bis(1,3-diketonato)copper(II) complexes (**2a-h**) and bis(1,3-diketonato)dioxouranium(VI) complexes (**3a-f**) and their electrophilic substitution reactions *i.e.*, bromination (**4a-e**) and nitration (**5a-e**) are reported in the present communication.



Ar = 4-BrC_6H_4; 4-ClC_6H_4; 4-FC_6H_4; 3-Cl, 4-FC_6H_3.

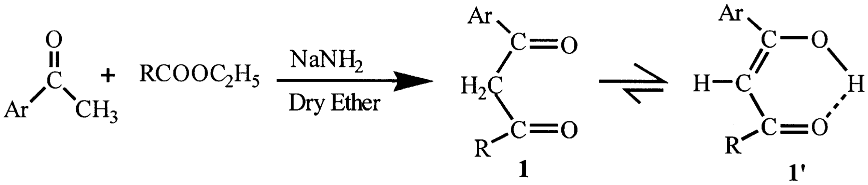
R = CH_3, CH_2F, C_2F_5. n = 2, 3, 4

Figure 1. 1,3-Diketones and their metal chelates.

RESULTS AND DISCUSSION

Synthesis of 1-Substituted-aryl-1,3-diketones and 1-Fluoroaryl-1,3-diketones (1a-h)

The condensation of appropriately substituted methyl ketone with an appropriate ester in the presence of sodamide afforded the desired 1-substituted-aryl-1,3-diketones and l-fluoroaryl-1,3-diketone (Fig. 2; (**1a-h**)). The 1-fluoroaryl-1,3-diketones (**1f-h**) are new while tie 1-chlorophenyl-l,3-diketone (**1b**) has been reported earlier but by a different procedure[22]. The IR spectra of β-diketones showed a very strong band in the 1640–1538 cm^{-1} region. This band was assigned to the C=O (enol) vibration. In all the fluorinated β-diketones, very strong absorption bands were observed in the 1345–1110 cm^{-1} region and were assigned due to C-F vibrations. No band was observed in the usual conjugated ketone region 1695–1672 cm^{-1} for



Ar = 4-BrC_6H_4; 4-ClC_6H_4; 4-FC_6H_4; 3-Cl, 4-FC_6H_3.

R = CH_3, CH_2F, C_2F_5.

Figure 2. Synthesis of 1-substituted-aryl-1,3-diketones.

either compound. These analytical and spectroscopic data of 1-fluoroaryl-1,3-diketones are in agreement with the data reported from our laboratory and/or elsewhere[3,16,18,19,21–23,25].

All compounds synthesized (**1a-h**) along with their physical characteristics, analytical analyses are recorded in Table I.

Synthesis of Bis(1,3-diketonato)copper(II) Complexes (2a-h)

The bis(1,3-diketonato)copper(II) complexes (Fig. 3; (**2a-h**)) have been prepared by adding a hot filtered solution of cupric acetate to a methanolic solution of appropriately substituted-aryl-1,3-diketones.

The IR spectra of these complexes (**2a-h**) show two very strong absorption bands between 1617 and 1542 cm^{-1} which are assigned mainly to the $>$C=O stretching mode. The third strong bands between 1538 and 1492 cm^{-1} are the $>$C=C$<$ stretching modes coupled slightly with the C-H in-plane bending mode. The absorption bands around 1460–1425 cm^{-1} are assigned to the degenerate symmetric deformation of the methyl group. The bands between 1280 and 1156 cm^{-1} are $>$C=C$<$ stretchings slightly coupled with the C-CH_3 stretching mode and C-H in-plane bending mode. The bands between 1020 and 1080 cm^{-1} are assigned to the C-F stretching mode. The bands between 748 and 677 cm^{-1} are assigned to a ring deformation coupled with both the Cu-O stretching and C-CH_3 stretching modes and the Cu-O stretching coupled slightly with the C-CH_3 bending mode. The bands between 500–400 cm^{-1} may be assigned to the pure Cu-O stretching mode.

All compounds synthesized (**2a-h**), along with their physical characteristics and analyses are recorded in Table II.

Synthesis of Bis(1,3-diketonato)dioxouranium(VI) Complexes (3a-f)

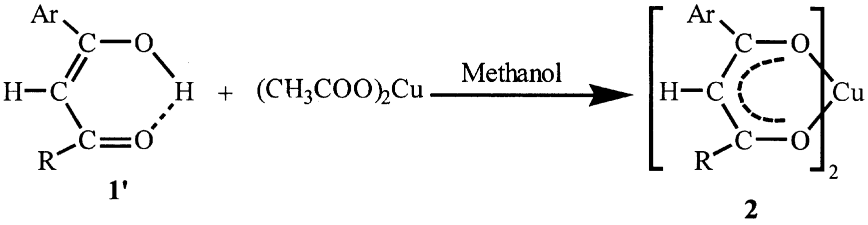
The bis(1,3-diketonato)dioxouranium(VI) complexes (Fig. 4; (**3a-f**)) have been prepared by heating the solution of the substituted-aryl-1,3-diketone and uranyl acetate dihydrate in ethanol.

The IR spectra of these complexes (**3a-f**) show prominent absorption bands at 1600–1552 cm^{-1} which are attributed to $>$C=O and $>$C=C$<$ stretching modes, respectively. The absorption bands between 1264–1100 cm^{-1} are assigned to the C-H in-plane bending mode. The absorption bands in the region of 920–964 cm^{-1} and 850–790 cm^{-1} are attributed to O=U=O (asym) and O=U=O (sym), respectively.

All compounds synthesized (**3a-f**), along with their physical characteristics and analyses are recorded in Table III.

Table I. Characteristics and Analytical Data of 1-Substituted-aryl-1,3-diketones (**1a-h**)

Compd. No.	Substituent(s) in Ar	R	Yield (%)	M. p. (°C)	Molecular Formula	Formula Weight	Analyses, Calc (Found)		Ref. No.
							C (%)	H (%)	
(**1a**)	4-Br	CH_3	72.24	91–92	$C_{10}H_9BrO_2$	241	49.79 (49.90)	3.73 (3.82)	21
(**1b**)	4-Cl	CH_3	90.04	90	$C_{10}H_9ClO_2$	196.5	61.06 (61.31)	4.58 (4.69)	22
(**1c**)	4-F	CH_3	80.20	43–44	$C_{10}H_9FO_2$	180	66.66 (66.50)	5.00 (5.17)	23
(**1d**)	3-Cl, 4-F	CH_3	79.80	48–50	$C_{10}H_8ClFO_2$	214.5	55.94 (56.04)	3.73 (3.85)	23
(**1e**)	4-F	C_2F_5	98.63	53	$C_{11}H_6F_6O_2$	284	46.48 (46.62)	2.11 (2.25)	25
(**1f**)	3-Cl, 4-F	C_2F_5	91.02	32–34	$C_{11}H_5ClF_6O_2$	318.5	41.44 (41.51)	1.57 (1.45)	New
(**1g**)	4-F	CH_2F	80.2	Highly Viscous	$C_{10}H_8F_2O_2$	198	60.60 (60.71)	4.04 (4.12)	New
(**1h**)	3-Cl, 4-F	CH_2F	79.80	Highly Viscous	$C_{10}H_7ClF_2O_2$	232.5	51.61 (51.65)	3.01 (3.21)	New



Ar = 4-BrC$_6$H$_4$; 4-ClC$_6$H$_4$; 4-FC$_6$H$_4$; 3-Cl, 4-FC$_6$H$_3$.

R = CH$_3$, CH$_2$F, C$_2$F$_5$.

Figure 3. Synthesis of bis(1,3.diketonate)copper(II).

Bromination of Bis(1,3-diketonato)dioxouranium(VI) Complexes (4a-e)

Bromination of the complexes is effected by refluxing a mixture of bis(1,3-diketonato)dioxouranium(VI) (Fig. 5; (**3a-e**)) and N-bromosuccinimide in chloroform without any catalyst.

The disappearance of C-H in-plane bending vibrations seen in the diketonate uranium complexes (**3a-e**) from the region of 1264–1100 cm^{-1} provides strong evidence for bromine attaching to the central carbon of the chelating ring of the diketone moiety. Besides this, the appearance of an additional band in the 550–500 cm^{-1} region due to C-Br also gives strong evidence for bromination of the uranyl complexes.

All compounds synthesized (**4a-e**) along with their physical characteristics, analytical analyses are recorded in Table V.

Nitration of Bis(1,3-diketonato)dioxouranium(VI) Complexes (5a-e)

The nitration of bis(1,3-diketonato)dioxouranium(VI) (Fig. 6; (**3a-e**)) is accomplished by treating bis(1,3-diketonato)dioxouranium(VI) (**3a-e**) with cupric nitrate trihydrate and acetic anhydride.

The active electrophile, nitronium ion, for this reaction is generated from acetyl nitrate as shown below:

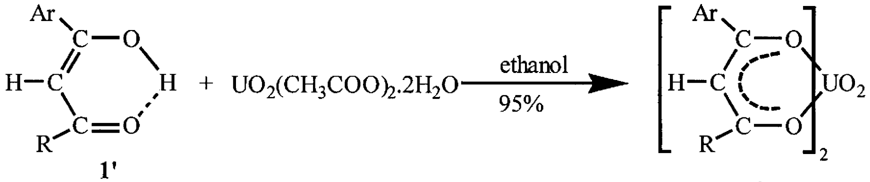
$$\mathrm{Cu(NO_3)_2\cdot 3H_2O + Ac_2O \longrightarrow AcONO_2}$$

$$\mathrm{AcONO_2 \rightleftharpoons AcO^- + NO_2^+}$$

The disappearance of the C-H in-plane bending vibrations from the region 1264–1100 cm^{-1} provides strong evidence for nitration of both chelate

Table II. Characteristics and Analytical Data of Copper Chelates (**2a-h**)

Compd. No.	Substituent in Ar	R	Yield (%)	M. p. (°C)	Molecular Formula	Formula Weight	Analyses, Calc (Found) C (%)	H (%)	Cu (%)	Ref. No.
(**2a**)	4-Br	CH_3	64	289–291	$C_{20}H_{16}Br_2O_4Cu$	543.5	44.16 (44.13)	2.94 (2.68)	11.68 (11.46)	21
(**2b**)	4-Cl	CH_3	62	308–310	$C_{20}H_{16}Cl_2O_4Cu$	454.5	52.80 (52.65)	3.52 (3.43)	13.97 (13.52)	–
(**2c**)	4-F	CH_3	68	238–240	$C_{20}H_{16}F_2O_4Cu$	421.5	56.94 (55.80)	3.79 (3.67)	15.06 (14.98)	23
(**2d**)	3-C, 4-F	CH_3	72	160–161	$C_{20}H_{14}Cl_2F_2O_4Cu$	490.5	48.93 (48.64)	2.85 (2.64)	12.94 (12.46)	23
(**2e**)	4-F	C_2F_5	40	254–255	$C_{22}H_{10}F_{12}O_4Cu$	629.5	41.94 (40.96)	1.59 (1.46)	10.09 (9.85)	25
(**2f**)	3-Cl, 4-F	C_2F_5	56	211–212	$C_{22}H_8Cl_2F_{12}O_4Cu$	698.5	37.80 (37.55)	1.14 (1.08)	9.09 (8.86)	New
(**2g**)	4-F	CH_2F	62	> 360	$C_{20}H_{14}F_4O_4Cu$	457.5	52.46 (51.87)	3.06 (2.98)	13.88 (13.38)	New
(**2h**)	3-Cl, 4-F	CH_2F	58	157–159	$C_{20}H_{12}Cl_2F_4O_4Cu$	526.5	45.58 (45.23)	2.28 (2.23)	12.06 (11.85)	New



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Ar = 4-BrC_6H_4; 4-ClC_6H_4; 4-FC_6H_4; 3-Cl, 4-FC_6H_3.

R = CH_3, C_2F_5.

Figure 4. Synthesis of bis(1,3-diketonato)dioxouranium(VI).

rings. The appearance of three additional absorption bands in the 1580–1550, 1365–1350 and 825–800 cm^{-1} regions are attributed to asymmetric and symmetric NO_2 stretching modes and C-N or N-O vibration mode.

All synthesized compounds (**5a-e**) along with their physical characteristics and analytical data are recorded in Table VI.

Similarly, the disappearance of the resonance signal due to methine C-H from the region of 6.2 ppm of bis(1,3-diketonato)dioxouranium(VI) (**3a-e**) is also in agreement with the effected bromination and nitration at the central carbon atom of the chelate ring. Substitution in the phenyl ring is unlikely because of electron release and the resonance effect of the coplanar phenyl ring.

EXPERIMENTAL

IR spectra were recorded using a Perkin-Elmer model 557 and a Nikolet Magna model-750 spectrophotometer in KBr pellets at the Central Drug Research Institute, Lucknow and Department of Chemistry, University of Rajasthan, Jaipur. ^1H NMR spectra were recorded on a Jeol FX-90 Q at 89.55 Hz in $CDCl_3$ solution with TMS as an internal standard. Melting points are uncorrected.

Preparation of 1-Substituted-aryl-1,3-butanedione (1a-h)

The title compounds (Table I; (**1a-h**)) were prepared by the method of Joshi *et al.*[25] To a stirred solution of sodamide (1.95 g, 50 mmol) in dry ether (50 mL) was added a solution of aryl methyl ketone (25 mmol) in dry ether (50 mL) and after 2 hours the calculated amount of the appropriate ester (25 mmol) (*i.e.*, ethyl acetate (2.2 g), or ethyl fluoroacetate (2.65 g), or ethyl pentafluoropropionate (4.8 g)) in dry ether (25 mL) was added. The resulting

Table III. Characteristics and Analytical Data of Bis(1,3-diketonato)dioxouranium(VI) (**3a-f**)

Compd. No.	Substituent in Ar	R	Yields (%)	M. p. (°C)	Formula Weight	Molecular Formula	Analyses, Calc (Found)		
							C(%)	H(%)	U(%)
(**3a**)	4-Br	CH_3	82.15	151–152	750	$C_{20}H_{16}Br_2O_6U$	32.00 (32.17)	2.13 (2.28)	31.73 (32.06)
(**3b**)	4-Cl	CH_3	84.80	247–248	661	$C_{20}H_{16}Cl_2O_6U$	36.31 (36.42)	2.42 (2.55)	36.00 (36.11)
(**3c**)	4-F	CH_3	89.35	228–230	628	$C_{20}H_{16}F_2O_6U$	38.22 (38.18)	2.55 (2.65)	37.90 (38.06)
(**3d**)	3-Cl, 4-F	CH_3	80.33	145–146	697	$C_{20}H_{14}Cl_2F_2O_6U$	34.43 (34.48)	2.01 (2.11)	34.15 (33.89)
(**3e**)	4-F	C_2F_5	88.75	160–162	836	$C_{22}H_{10}F_{12}O_6U$	31.58 (31.72)	1.20 (1.31)	28.47 (28.61)
(**3f**)	3-Cl, 4-F	C_2F_5	83.19	137–139	905	$C_{22}H_8Cl_2F_{12}O_6U$	29.17 (30.66)	0.88 (1.22)	26.30 (26.70)

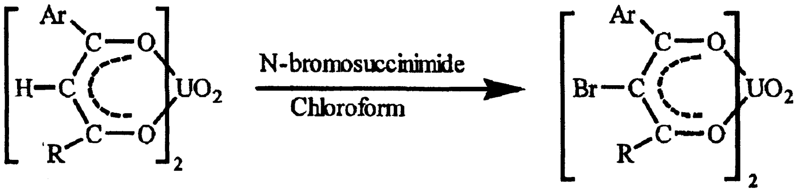

Figure 5. Bromination of bis(1,3-diketonato)dioxouranium(VI).

Table IV. IR Data of Bis(1,3-diketonato)dioxouranium(VI) (ν_{max} Values in cm^{-1})

Compd. No.	C=O Stretching	C=C Stretching	C-H In-plane bending	UO_2 (Asym)	UO_2(Sym)
(**3a**)	1586 vs	1532 vs	1178 m	962 m	844 s
(**3b**)	1588 vs	1534 vs	1212 m	962 m	846 s
(**3c**)	1604 vs	1532 vs	1234 m	964 m	854 s
(**3d**)	1596 vs	1530 vs	1264 m	964 m	832 s
(**3e**)	1600 vs	1500 vs	1190 m	920 m	790 s
(**3f**)	1600 vs	1500 vs	1200 m	940 m	800 s

solution was stirred and refluxed for 4 hours and then poured into hydrochloric acid (10%, 200 mL) and allowed to settle for 30 minutes. The resulting 1-substituted-aryl-1,3-butanedione (**1a-h**) was extracted with chloroform, washed with water (3 × 50 mL) and dried over sodium sulphate. Chloroform was distilled off and the 1-substituted-aryl-1,3-butanedione (**1a-h**) was recrystallized from petroleum ether (b. p. 60–80 °C).

Preparation of Bis(1,3-diketonato)copper(II) (2a-h)

To a methanolic solution of substituted-aryl- 1,3-diketone (25 mmol) was added a hot filtered solution of cupric acetate (40 g, in 250 mL water) and the mixture was allowed to cool to room temperature. The resulting bis(1,3-diketonato) copper(II) (Table II; (**2a-h**)) was filtered, dried, washed with petroleum ether (100 mL, b. p. 60–80 °C) and recrystallized from chloroform.

Preparation of Bis(1,3-diketonato)dioxouranium(VI) (3a-f)

These compounds (Table III; (**3a-f**)) were prepared by the method of Das[24]. A hot filtered solution of uranyl acetate dihydrate (1.50 g, 3.53 mmol in

Table V. Analytical Data and Physico-Chemical Properties of Derivative of Bis(2-bromo-1,3-diketonato)dioxouranium(VI) (**4a-e**)

Compd. No.	Substituent in Ar	R	Yield (%)	M. p. (°C)	Formula Weight	Molecular Formula	Analyses, Calc (Found)		
							C (%)	H (%)	U (%)
(**4a**)	4-Br	CH_3	76.25	281–282 dec.	908	$C_{20}H_{14}Br_4O_6U$	26.43 (26.65)	1.54 (1.64)	26.21 (26.54)
(**4b**)	4-Cl	CH_3	83.34	> 360	819	$C_{20}H_{14}Br_2Cl_2O_6U$	29.30 (29.57)	1.71 (1.91)	29.06 (29.39)
(**4c**)	4-F	CH_3	88.51	251–252 dec.	786	$C_{20}H_{14}Br_2F_2O_6U$	30.53 (30.72)	1.78 (1.88)	30.28 (30.68)
(**4d**)	3-Cl, 4-F	CH_3	76.21	> 360	855	$C_{20}H_{12}Br_2Cl_2F_2O_6U$	28.07 (28.23)	1.40 (1.56)	27.84 (28.05)
(**4e**)	4-F	C_2F_5	80.29	> 360	994	$C_{22}H_8Br_2F_{12}O_6U$	26.56 (26.87)	0.80 (1.09)	23.94 (24.15)

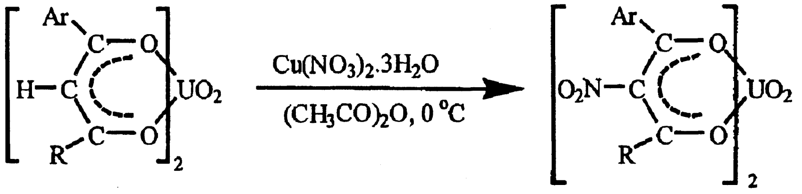

Figure 6. Nitration of bis(1,3-diketonate)dioxouraniun(VI).

25 mL water) was added dropwise with constant stirring to a solution of substituted-aryl-1,3-diketone (7.06 mmol in 25 mL ethanol). The reaction mixture was digested for 10 minutes and then cooled in an ice bath. The resulting orange products were filtered and washed with aqueous ethanol (50%, 3 × 20 mL). Recrystallization of the product was carried out with chloroform.

Electrophilic Substitution Reactions

Substitution reactions of bis(1,3-diketonato)dioxouranium(VI) (**3a-e**) were carried out by the method of Joshi *et al.*[25] The methine proton of the central carbon atom of the chelate ring was subjected to bromination and nitration.

Bromination of Bis(1,3-diketonato)dioxouranium(VI) (4a-e)

To a solution of bis(1,3-diketonato)dioxouranium(VI) (**3a-e**) (1 mmol) in chloroform (25 mL) was added N-bromosuccinimde (0.534 g, 3 mmol) and the solution was refluxed for 4–7 hours. The solvent was removed and the solid thus obtained was collected. Subsequently, it was washed several times with a solution of sodium hydroxide (2%, 3 × 20 mL), dried and collected (Table V; (**4a-e**)).

Nitration of Bis(1,3-diketonate)dioxouranium(VI) (5a-e)

The nitration of bis(1,3-diketonato)dioxouranium(VI) (**3a-e**) was carried out under mild conditions. A cooled solution of bis(1,3-diketonato)-dioxouranium(VI) (**3a-e**) (1 mmol) in acetic anhydride (5 mL) was added dropwise with constant stirring to cupric nitrate trihydrate (0.7248 g, 3 mmol) in acetic anhydride (5 mL) and kept at 0 to −5 °C for 5 to 15 hours.

Table VI. Characteristics and Analytical Data Bis(2-nitro-1,3-diketonato)dioxouranium(VI) (**5a-e**)

Compd. No.	Substituent in Ar	R	Yield (%)	M. p. (°C)	Formula Weight	Molecular Formula	Analyses, Calc (Found)		
							C (%)	H (%)	U (%)
(**5a**)	4-Br	CH_3	75.46	210–211	840	$C_{20}H_{14}Br_2N_2O_{10}U$	28.57 (28.70)	1.67 (1.72)	28.33 (28.71)
(**5b**)	4-Cl	CH_3	82.59	220–221	751	$C_{20}H_{14}C_{12}N_2O_{10}U$	31.96 (32.13)	1.86 (2.01)	31.69 (31.85)
(**5c**)	4-F	CH_3	74.29	84–85	718	$C_{20}H_{14}F_2N_2O_{10}U$	33.43 (33.52)	1.95 (2.06)	33.15 (33.42)
(**5d**)	3-Cl, 4-F	CH_3	88.94	98–99	787	$C_{20}H_{12}Cl_2F_2N_2O_{10}U$	30.49 (30.42)	1.52 (1.74)	30.24 (30.52)
(**5e**)	4-F	C_2F_5	79.06	282 dec.	926	$C_{22}H_8F_{12}N_2O_{10}U$	28.51 (28.69)	0.86 (1.04)	25.70 (25.91)

The reaction mixture was then treated with an ice-cold aqueous solution of sodium acetate (8.2 g, 100 mmol in 25 mL of water). The precipitate thus obtained was extracted with chloroform, washed with water (3 × 50 mL) and dried. The residue after evaporation of chloroform was recrystallized from ethyl acetate and dried under vacuum (Table VI; (**5a-e**)).

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