

## Synthesis and characterization of thorium and uranium cyanoacetates and their coordination compounds

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**Abstract.** Tetracyanoacetates of thorium and uranium,  $M(\text{NCCH}_2\text{COO})_4$  (where  $M = \text{Th}$  or  $\text{U}$ ) and dioxouranium (VI) dicyanoacetate  $[\text{UO}_2(\text{NCCH}_2\text{COO})_2 \cdot \text{H}_2\text{O}]$  and their coordination complexes with dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), 1,10 phenanthroline (Phen) and 2,2'-bipyridyl (Bipy) have been synthesised and characterised by elemental analysis, molecular weight determination, molar conductance measurements, X-ray diffraction and infrared spectroscopic studies ( $4000\text{--}200\text{ cm}^{-1}$ ). Structural aspects of the compounds and the sites of bonding of the ligands to the central metal atom have been discussed in the light of shifts in the  $\nu(\text{C}\equiv\text{N})$ ,  $\nu(\text{COO})$ ,  $\nu(\text{UO}_2)$  and the metal-ligand stretching vibrations. Thermogravimetric analysis of the compounds have been carried out to study thermal decomposition modes.

**Keywords.** Thorium cyanoacetate; uranium cyanoacetate; coordination complexes.

### 1. Introduction

Although acetates of uranium and their complexes have been studied in recent years (Markov and Tsapkin 1962; Paul *et al* 1965; Singh and Singh 1983; Ahuja *et al* 1987), much less is known about their substituted acetates like the cyanoacetates where the substituent cyano group itself is a potential donor site in addition to the usual carboxylate group. The objective of the present work on the cyanoacetates of uranium and thorium is to investigate how the presence of the electron-withdrawing cyano group modifies the coordination behaviour of the carboxylate group towards uranium and thorium. It was considered interesting to see if the cyanoacetates can further extend their coordination sphere by forming adducts with common bidentate or monodentate ligands such as 2,2'-bipyridyl (Bipy), 1, 10 phenanthroline (Phen), DMF and DMSO.

### 2. Experimental

Chemicals  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{UCl}_4$  were prepared and purified by suitable methods. Pure ligands were obtained commercially (Aldrich Chemicals) and used without further purification. The solvents tetrahydrofuran (THF), acetonitrile ( $\text{CH}_3\text{CN}$ ), *N,N*-dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) were treated with appropriate drying agents and fractionally distilled before use.

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## 2.1 Preparation of compounds

2.1a  $Th(NCCH_2COO)_4$ : Thorium tetracyanoacetate was prepared by dissolving freshly precipitated  $Th(CO_3)_2$  (obtained by the reaction of  $(NH_4)_2CO_3$  with  $Th(NO_3)_4$  in an aqueous medium) in aqueous cyanoacetic acid solution. The solution was subjected to slow evaporation under *vacuo* till  $Th(NCCH_2COO)_4$  crystallized out. The compound was filtered off, washed with methanol and dried in *vacuo* for several hours at room temperature.

2.1b  $U(NCCH_2COO)_4$ : Uranium tetracyanoacetate was prepared by the reaction of  $UCl_4$  and Na-cyanoacetate (1:4) in THF. A greenish-yellow compound was obtained from the filtrate after concentrating it in *vacuo* and adding *n*-pentane to the concentrate. All operations were carried out in a glove box continuously flushed with dry nitrogen. An attempt to prepare  $U(NCCH_2COO)_4$  by direct interaction of  $UCl_4$  and cyanoacetic acid (1:4) in  $CH_2Cl_2$  resulted in the formation of  $UCl_2(NCCH_2COO)_2(NCCH_2COOH)$ .

2.1c  $NH_2[UO_2(NCCH_2COO)_3]$ : Ammonium uranyl tris-cyanoacetate was formed when the freshly precipitated  $(NH_4)_2U_2O_7$  [precipitated by the reaction of  $NH_4OH$  on  $UO_2(NO_3)_2$  in water] was dissolved in the minimum amount of cyanoacetic acid solution in water. The product was crystallized out from the solution by partial evaporation of the solvent in *vacuo*. The compound was filtered, washed with methanol and dried under reduced pressure.

2.1d  $[UO_2(NCCH_2COO)_2 \cdot H_2O]$ : Uranyl cyanoacetate was prepared by dissolving the freshly precipitated  $UO_3$  [precipitated by adding  $C_5H_5N$  to an aqueous solution of  $UO_2(NO_3)_2$ ] in the minimum amount of cyanoacetic acid solution. The compound was crystallized out from the reaction mixture.

2.1e  $[UO_2(NCCH_2COO)_2 \cdot L]$ , ( $L = Bipy/Phen$ ): The adducts were prepared by the interaction of  $UO_2(NCCH_2COO)_2 \cdot H_2O$  and the ligand (1:1 mole) in 50% (v/v) water-methanol solution. The compounds crystallized out from the reaction mixture on slow evaporation.

2.1f  $[UO_2(NCCH_2COO)_2 \cdot DMSO]$ ,  $[Th(NCCH_2COO)_4 \cdot L]$ ,  $L = DMSO$  or  $DMF$ : In general, the adducts were prepared by dissolving  $UO_2(NCCH_2COO)_2 \cdot H_2O$  or  $Th(NCCH_2COO)_4$  in the respective ligands. After stirring for 4 to 5 h at room temperature the excess ligand was pumped out under reduced pressure and the product dried in *vacuo*.

## 2.2 Analysis

Metal content in the compounds was determined gravimetrically as  $U_3O_8$  or  $ThO_2$ . Microanalysis for carbon, hydrogen and nitrogen was carried out by the Analytical Chemistry Division of our Research Centre. The analytical results are given in table 1.

## 2.3 Physicochemical studies

The infrared spectra ( $4000-200\text{ cm}^{-1}$ ) of the compounds were recorded on a Perkin-

Table 1. Elemental analysis.

Compound	Colour	Melting point (°C)	Metal found (calc) (%)	Carbon found (calc) (%)	Hydrogen found (calc) (%)	Nitrogen found (calc) (%)
U(NCCH <sub>2</sub> COO) <sub>4</sub>	Greenish yellow	~ 150 D	40.8 (41.46)	24.6 (25.09)	1.50 (1.39)	9.50 (9.76)
UCl <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub> ·* NCCH <sub>2</sub> COOH]	Brown	~ 110 D	42.0 (42.35)	18.8 (19.21)	1.32 (1.24)	8.01 (7.47)
Th(NCCH <sub>2</sub> COO) <sub>4</sub>	White	~ 220 D	41.0 (40.84)	24.8 (25.32)	1.38 (1.41)	9.38 (9.85)
Th(NCCH <sub>2</sub> COO) <sub>4</sub> ·DMSO	White	~ 180 D	37.3 (37.77)	25.8 (26.16)	2.59 (2.18)	8.16 (8.72)
Th(NCCH <sub>2</sub> COO) <sub>4</sub> ·DMF	White	~ 160 D	37.38 (36.18)	27.6 (28.08)	2.13 (2.33)	10.49 (10.91)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	Yellow	~ 110 D	51.8 (52.19)	15.5 (15.79)	1.40 (1.32)	6.08 (6.14)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub> ·Bipy	Yellow	~ 200 D	39.9 (40.05)	32.3 (31.92)	2.02 (1.98)	9.42 (9.38)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub> ·Phen	Yellow	~ 205 D	39.0 (38.57)	33.9 (34.95)	1.97 (1.94)	9.67 (9.06)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub> ·DMSO	Yellow	~ 105 D	46.2 (46.11)	17.5 (18.60)	2.01 (1.94)	6.06 (5.22)
NH <sub>4</sub> [UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>3</sub> ]	Yellow	~ 130 D	44.8 (44.70)	19.8 (20.00)	2.54 (1.85)	11.05 (10.37)

D = decomposed without melting; \* Cl(%) – found 12.2, calc. 12.64.

Elmer grating spectrophotometer model 577, using cesium iodide optics, both in nujol and fluorolube. The relevant IR bands are reported in table 2.

Molar conductance of the compounds in CH<sub>3</sub>CN, DMSO or DMF were measured at room temperatures with a Toshniwal Digital Conductivity Meter (type CL01-01 A) using a dip type cell. Conductivity measurements were carried out on 10<sup>-3</sup> M solutions of the compounds. Molecular weights of the compounds were taken to be equal to the empirical formula for calculating molar conductance.

Thermogravimetric measurements of representative compounds were carried out on a stanton thermobalance in air (2.5 l h<sup>-1</sup>) keeping the sample weight ≈ 200 mg and a heating rate of 4 K min<sup>-1</sup>. Stable intermediate phases were isolated in separate experiments and identified by percentage weight loss and IR studies. The results are included in table 3.

### 3. Results and discussion

Analytical results of the compounds are reported in table 1. None of the compounds has a melting point but they all decompose and turn black when heated in a sealed capillary. The compounds are insoluble in inert organic solvents such as benzene, chloroform, carbontetrachloride, hexane etc. but they dissolve readily in water, and

Table 2. Selected infrared bands of the compounds in nujol ( $\text{cm}^{-1}$ ).

U(cyac) <sub>4</sub>	Th(cyac) <sub>4</sub>	Th(cyac) <sub>4</sub> DMSO	Th(cyac) <sub>4</sub> DMF	UO <sub>2</sub> (cyac) <sub>2</sub> H <sub>2</sub> O	UO <sub>2</sub> (cyac) <sub>2</sub> Bipy	UO <sub>2</sub> (cyac) <sub>2</sub> Phen	UO <sub>2</sub> (cyac) <sub>2</sub> DMSO	NH <sub>4</sub> [UO <sub>2</sub> (cyac) <sub>3</sub> ]	Assignment
2300 m	2300 m	2300 m	2300 m	2305 s	2300 m	2300 m	2300 m	2300 m	$\nu(\text{C} \equiv \text{N})$
1610 vs	1705 s	1705 s	1710 s	1720 sb	1670 sh	1665 s	1680 vs	1690 sb	$\nu_{\text{as}}(\text{COO})$
1570 s	1565 s	1615 s	1615 s	1630 s	1630 s	1590 s	1580 sh	1580 sb	
	1580 s	1580 s	1570 s	1580 s	1600 s				
	1560 s			1585 s	1585 s				
1430 vs	1440 s	1440 s	1440 s	1440 s	1435 s	1440 s	1440 ms	1410 s	$\nu_{\text{sy}}(\text{COO})$
1410 sh	1420 s	1410 sh	1410 s	1400 s	1410 sh	1410 ms	1400 s		
—	—	—	—	930 s	945 s	940 vs	935 vs	925 vs	$\nu_3(\text{UO}_2)$
—	—	—	—	840 m	840 mw	850 ms	840 m	825 mw	$\nu_1(\text{UO}_2)$
445 m	430 m	435 m	435 m	440 m	440 w	425 m	470 s	440 sh	$\nu(\text{M}-\text{O}), \text{ligand}$
410 m	410 m	400 m	400 m	400 m	400 m	390 m	445 s	410 sh	
				380 m			400 ms	400 m	
300 m	295 sh	320 w	285 sh	300 sh	290 m	285 sh	305 m	315 m	$\nu(\text{M}-\text{N}), \text{cyano}$
285 s	280 s	285 sh	285 s	280 sb	270 s	270 m	285 s	280 sh	$\nu(\text{M}-\text{N}), \text{ligand}$
					510 w	520 m			$\nu(\text{O}-\text{H})$
					490 w	505 m			
				3400 s					$\delta(\text{H}-\text{O}-\text{H})$
				3200 s					$\nu(\text{S}=\text{O})\text{DMSO}$
				1600 s					$\nu(\text{C}=\text{O})\text{DMF}$
		1030 s	1650 s				1035 s		

(cyac) = (NCCH<sub>2</sub>COO)<sub>x</sub>; s = strong; m = medium; b = broad; v = very; sh = shoulder; w = weak.

Table 3. Thermal analysis of results.

Compound	Step	Temperature range (°C)	Solid product	% Weight loss found (calc)
U(NCCH <sub>2</sub> COO) <sub>4</sub>	1	110–200	UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub>	23.0(23.43)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub>	2	200–550	1/3 U <sub>3</sub> O <sub>8</sub>	35.6(35.92)
Th(NCCH <sub>2</sub> COO) <sub>4</sub>	1	200–300	ThO <sub>2</sub>	54.2(53.52)
Th(NCCH <sub>2</sub> COO) <sub>4</sub> ·DMF	1	150–200	Th(NCCH <sub>2</sub> COO) <sub>4</sub>	10.3(11.38)
Th(NCCH <sub>2</sub> COO) <sub>4</sub>	2	200–300	ThO <sub>2</sub>	54.0(53.52)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub> ·DMSO	1	120–200	UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub>	14.8(15.12)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub>	2	200–550	1/3 U <sub>3</sub> O <sub>8</sub>	35.0(35.92)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub> ·Phen	1	180–200	UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub>	28.0(29.13)
UO <sub>2</sub> (NCCH <sub>2</sub> COO) <sub>2</sub>	2	200–550	1/3 U <sub>3</sub> O <sub>8</sub>	36.5(35.92)

can be recovered from water. An attempt to determine molecular weight using water as solvent by the cryoscopic method suggests strong dissociation. Molar conductance measurements of the compounds in water, DMSO and acetonitrile solutions showed them to be nonelectrolytes (except the compound NH<sub>4</sub>[UO<sub>2</sub>(NCCH<sub>2</sub>COO)<sub>3</sub>] which ionized as NH<sub>4</sub><sup>+</sup> + UO<sub>2</sub>(NCCH<sub>2</sub>COO)<sub>3</sub><sup>-</sup>).

### 3.1 Infrared spectra

The cyanoacetate ion NCCH<sub>2</sub>COO<sup>-</sup> has two donor groups, the carboxylate group and the cyanogroup. Besides bridging two metal atoms, a carboxylate group can also act as a monodentate or a bidentate chelate (Vaidya *et al* 1988; Vaidya and Jain 1989). A cyano group also has two possible modes of bonding, either through the  $\sigma$ -electrons or through the  $\pi$ -electrons of the triple bond (Jain and Rivest 1967). Infrared spectral studies have yielded useful information about the sites and nature of bonding of the C $\equiv$ N and COO groups in the compounds. The shifts in  $\nu(\text{COO})$  and their magnitude of separation ( $\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{sy}}(\text{COO})$ ) are related to the nature of bonding of the carboxylate group (Garner and Hughes 1975). In monodentate coordination, the C–O bond becomes inequivalent and the  $\nu_{\text{as}}(\text{COO})$  increases from its free ion value as the vibration takes on a more ketonic form. For ionic sodium cyanoacetate the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{sy}}(\text{COO})$  bands are reported at 1596 and 1422 cm<sup>-1</sup> respectively (Sinha and Katon 1972). Thus for compounds having monodentate COO groups, the value is expected to be of much higher order (Linglard and Rau 1953).

Infrared spectra of U(NCCH<sub>2</sub>COO)<sub>4</sub> and Th(NCCH<sub>2</sub>COO)<sub>4</sub> display two  $\nu_{\text{as}}(\text{COO})$  bands in the region 1565 to 1610 cm<sup>-1</sup> and two  $\nu_{\text{sy}}(\text{COO})$  bands in the region 1400 to 1440 cm<sup>-1</sup>. The existence of these doublets suggests two types of coordinated COO groups in the compounds. The magnitude of separation of these bands ( $\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{sy}}(\text{COO})$ ) lies in the range of 170 to 220 cm<sup>-1</sup> suggesting that the COO groups in these compounds are of the bidentate type (Vaidya *et al* 1988; Garner and Hughes 1975). The fact that the C $\equiv$ N shows a positive shift of  $\sim 50$  cm<sup>-1</sup> due to the coordinated cyano group through nitrogen and the carboxylate groups act as bidentate groups, strongly suggests that the NCCH<sub>2</sub>COO<sup>-</sup> acts as a tridentate group, bridging two metal atoms.

It is interesting to note that when Th(NCCH<sub>2</sub>COO)<sub>4</sub> is reacted with ligands like DMSO or DMF to obtain adducts of the type Th(NCCH<sub>2</sub>COO)<sub>4</sub>·L, the IR spectra of

the adducts show an additional strong band at  $\sim 1700\text{ cm}^{-1}$  which can be assigned to  $\nu_{\text{as}}(\text{COO})$  of a monodentate COO group. The magnitude of separation,  $\Delta\nu(\text{COO})(1710\text{--}1440\text{ cm}^{-1})$  of the order of  $270\text{ cm}^{-1}$  indicates that in the adducts some bidentate COO groups most probably acquire monodentate nature to accommodate the in-coming ligand e.g. DMSO or DMF.

When the adducts decompose to give the parent compounds as the intermediate, the additional band at  $1700\text{ cm}^{-1}$  observed for adducts disappears. A band at  $1030\text{ cm}^{-1}$  for  $[\text{Th}(\text{NCCH}_2\text{COO})_4 \cdot \text{DMSO}]$ , due to coordinated  $\nu(\text{S}=\text{O})$  against  $1080\text{ cm}^{-1}$  for free DMSO confirms bonding of DMSO through oxygen (Jain and Rivest 1969). Similarly a band at  $1650\text{ cm}^{-1}$  for  $[\text{Th}(\text{NCCH}_2\text{COO})_4 \cdot \text{DMF}]$  due to coordinated C=O against  $1680\text{ cm}^{-1}$  for free DMF suggests bonding through the carbonyl oxygen (Deshpande *et al* 1985).

Infrared spectra of all the uranyl cyanoacetate complexes display strong absorption bands at  $\sim 930\text{ cm}^{-1}$  due to  $\nu_3$  vibration of the  $\text{UO}_2$  group. Appearance of a  $\nu_1$  band at  $\sim 840\text{ cm}^{-1}$  implies that the linearity of the  $\text{O}=\text{U}=\text{O}$  group is not maintained in these compounds. In the carboxylate band region the uranyl compounds exhibit more than one type of  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{sy}}(\text{COO})$  bands. Separation of the order of  $280$  to  $240\text{ cm}^{-1}$  can be due to monodentate COO groups and the one of the order of  $200$  to  $150\text{ cm}^{-1}$  due to bidentate COO groups. Thus the uranyl cyanoacetate adducts under present study seem to have one monodentate COO and the other bidentate COO group as indicated by IR results. Though Bipy and Phen are potentially chelating ligands, under suitable steric conditions their monodentate action can not be ruled out. When Phen and Bipy form complexes with metal ions their IR spectra undergo changes (Sinha 1964; Vaidya and Jain 1989) particularly in the bands in the regions  $1400\text{--}1650\text{ cm}^{-1}$  (C=C and C=N ring stretching vibrations),  $950\text{--}1050\text{ cm}^{-1}$  (breathing modes) and  $750\text{--}850\text{ cm}^{-1}$  (C-H out-of-plane deformation). In the present case of  $[\text{UO}_2(\text{NCCH}_2\text{COO})_2 \cdot \text{Bipy}]$  the free ligand bands at  $1590$ ,  $1570$  and  $1550\text{ cm}^{-1}$  appear to have shifted to  $1600\text{--}1560\text{ cm}^{-1}$  in addition to the unshifted bands. The ring breathing mode at  $995\text{ cm}^{-1}$  in free Bipy which on chelation is expected to shift upwards remains unshifted. Moreover, the fact that monodentate ligands such as DMSO form only 1:1 adducts with  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  cyanoacetates indicates that most probably Bipy under the present circumstances behaves as a monodentate ligand though the support of single crystal X-ray data is required for confirmation.

The IR spectrum of  $[\text{UO}_2(\text{NCCH}_2\text{COO})_2 \cdot \text{Phen}]$  displays a large number of bands in the  $1600\text{--}1400\text{ cm}^{-1}$  region due to upward shifted and unshifted ligand bands. The  $615\text{ cm}^{-1}$  band in free Phen which is known to shift to higher frequency and intensify on chelation (Jain and Rivest 1970; Vaidya and Jain 1989) remains unchanged in the present case. This suggests that like Bipy, Phen also coordinates to uranyl cyanoacetate.

It is interesting to note that when a monodentate ligand such as DMSO forms a complex  $[\text{UO}_2(\text{NCCH}_2\text{COO})_2 \cdot \text{DMSO}]$ , the IR bands due to  $\nu\text{C} \equiv \text{N}$ ,  $\nu(\text{COO})$  and  $\nu(\text{UO}_2)$  remain almost identical to those of Bipy or Phen adducts. The  $\nu(\text{S}=\text{O})$  band is, however, lowered by  $35\text{ cm}^{-1}$  as a result of coordination of DMSO to uranium. Thus, on the basis of results discussed above, the uranyl cyanoacetate compounds can be assigned a polymeric structure.

In the low frequency region, in addition to the  $\text{O}=\text{U}=\text{O}$  bending mode at  $\sim 260\text{ cm}^{-1}$ , the IR spectra of the uranyl compounds show bands in the

300–260  $\text{cm}^{-1}$  and 450–400  $\text{cm}^{-1}$  regions, which can tentatively be assigned to  $\nu(\text{U-N})$  cyano and  $\nu(\text{U-O})$  carboxylate bands respectively. In the case of Bipy and Phen adducts the additional bands in the 500–520  $\text{cm}^{-1}$  region seem to be due to  $\nu(\text{U-N})$  Bipy or Phen bonding.

### 3.2 Thermogravimetric analysis

Thermogravimetric analysis of  $\text{U}(\text{NCCH}_2\text{COO})_4$  and  $\text{Th}(\text{NCCH}_2\text{COO})_4$  was carried out under identical conditions in air. It was interesting to note that while  $\text{U}(\text{NCCH}_2\text{COO})_4$  suffers thermal decomposition through the formation of  $\text{UO}_2(\text{NCCH}_2\text{COO})_2$  as an intermediate product which further decomposes rapidly to  $\text{U}_3\text{O}_8$  as the end product,  $\text{Th}(\text{NCCH}_2\text{COO})_4$  decomposed to  $\text{ThO}_2$  in a single step. The formation of  $\text{UO}_2(\text{NCCH}_2\text{COO})_2$  as an intermediate was confirmed by weight loss and its IR spectra, where characteristic  $\nu_3(\text{UO}_2)$  bands could distinctly be identified at 940  $\text{cm}^{-1}$ .

Thermal decomposition of the adducts of thorium cyanoacetate and uranyl cyanoacetate also proceeds in two stages. In the first stage the neutral ligand gets detached from the addition compound leaving the parent cyanoacetate  $\text{Th}(\text{NCCH}_2\text{COO})_4$  or  $\text{UO}_2(\text{NCCH}_2\text{COO})_2$  as intermediate product which further decomposes rapidly to the respective stable oxide in the second stage. The formation of intermediates was confirmed on the basis of their percentage weight loss and infrared spectra. The formation of  $\text{ThO}_2$  or  $\text{U}_3\text{O}_8$  as the end product was confirmed by percentage weight loss and X-ray powder patterns. The thermogravimetric results are given in table 3.

### 3.3 X-ray powder pattern

X-ray diffraction powder patterns taken for some of the compounds, using  $\text{CuK}_\alpha$  radiation, showed them to be highly crystalline, having low symmetry polyhedral structures. The X-ray results are included in table 4.

Table 4. X-ray data for U and Th compounds.

$\text{Th}(\text{cyac})_4$		$\text{UO}_2(\text{cyac})_2 \cdot n\text{H}_2\text{O}$		$\text{UO}_2(\text{cyac})_2 \cdot (\text{Phen})$		$\text{UO}_2(\text{cyac})_2 \cdot (\text{Bipy})$	
$d(\text{\AA})$	$\frac{I}{I_0} \times 100$	$d(\text{\AA})$	$\frac{I}{I_0} \times 100$	$d(\text{\AA})$	$\frac{I}{I_0} \times 100$	$d(\text{\AA})$	$\frac{I}{I_0} \times 100$
$\text{CuK}_\alpha$		$\text{CuK}_\alpha$		$\text{CuK}_\alpha$		$\text{CuK}_\alpha$	
10.652	11	6.6320	61	10.848	100	10.526	52
9.1650	100	6.5346	98	9.3585	19	9.0434	63
5.6802	26	5.7350	66	6.5107	17	8.3065	54
4.8478	16	4.6707	79	6.3937	20	6.4964	100
4.0042	12	4.3427	100	5.4049	13	5.5391	41
3.6187	15	3.6043	61	5.2002	11	5.2154	42
3.4269	13	2.9449	52	4.5177	9	5.0475	35
2.7631	13	2.6217	48	4.3427	9	4.0767	38

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