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Uranyl monopicolinate complexes

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Abstract

Reactions of Hmpa (pyridine-2-carboxylic acid) with $UO_2(NO_3)_2 \cdot 6H_2O$, under a variety of reaction conditions, result in the formation of $[UO_2(mpa)_2](Hmpa) \cdot 2.5H_2O$ (**I**), unless the relative concentrations of Hmpa and (NO_3^-) are controlled in order to precipitate $H_2O \cdot [UO_2(mpa)(H_2O)] \cdot [UO_2(NO_3)_2] \cdot [UO_2(mpa)(H_2O)] \cdot H_2O$ (**II**). The crystallographic details (XRD) for **II** are presented here, along with the infrared (IR), thermogravimetric (TG), differential thermal analysis (DTA), microanalysis (mA) and solid-state ^{13}C nuclear magnetic resonance (NMR) data for both products. © 1998 Published by Elsevier Science S.A.

Keywords: Carboxylate; Monopicolinate; Nitrate; Stoichiometry; Uranyl

1. Introduction

Mixed oxygen and nitrogen donor proligands have proved very successful in the selective binding and separation of the early actinides. The variety of modes of coordination (monodentate, bidentate or polydentate) of these organic compounds give rise to monomeric or dimeric species and to the development of linear chains, sheets and three-dimensional linkages through bridging atoms and extensive hydrogen-bonding networks [1–3]. Heterocyclic carboxylic acids have the potential to act as chelating ligands by the coordination of the ring heteroatom. For example, furoic acid (Hfra) has three coordinating sites. Coordination of the carboxylate oxygen atoms is well known [4–8] but the presence of the heterocyclic oxygen atom can restrict the bonding of the carboxylate group and can lead to the formation of a 5-membered chelate, involving one of the carboxylate oxygen atoms and the ring heteroatom, with the uranyl ion [9]. Evidence for chelation is found in the negative shifts of the asymmetric ν(C-O-C) stretching frequencies from 1200 and 1130 cm^{-1} to 1160 and 1080 cm^{-1} and the symmetric ν(C-O-C) from 890 and 850 cm^{-1} to 820 and 800 cm^{-1} and the appearance of new bands at 520 and 500 cm^{-1}, assigned to ν(U-O), in the IR spectrum. In a similar fashion, monopicolinic acid (Hmpa) is also capable of forming a 5-membered chelate through its heterocyclic nitrogen and a carboxylic oxygen atom, as well as having the potential to bridge uranyl centres using its other carboxylate oxygen donor atom.

There is only one crystallographically characterised uranyl compound containing monopicolinic acid [10]. This compound, bis(dipicolinato)dioxouranium monopicolinic acid hexahydrate $[UO_2(Hdpa)_2] \cdot Hmpa \cdot 6H_2O$, has a hexagonal bipyramidal coordination polyhedron at the uranium atom with ligating dipicolinate (1−) ligands. Thus the monopicolinic acid molecule is not directly bonded to the UO_2 moiety, its presence in the crystal lattice being a consequence of the synthetic pathway allowing a partial photolytic oxidative decarboxylation of a molecule of dipicolinic acid [11]. We present the X-ray diffraction data for the trinuclear uranyl species $H_2O \cdot [UO_2(mpa)(H_2O)] \cdot [UO_2(NO_3)_2] \cdot [UO_2(mpa)(H_2O)] \cdot H_2O$ (**II**), in which the monopicolinate groups are directly bonded to two of the metal centres and provide comparative IR, TG, DTA and NMR data to support the formulation of product **I** as $[UO_2(mpa)_2] \cdot (Hmpa) \cdot 2.5H_2O$.

2. Experimental details

$UO_2(NO_3)_2 \cdot 6H_2O$ (0.5 g 1 mmol), purchased from the Aldrich Chemical Company, was dissolved in H_2O (20 cm^3) and reacted with Hmpa (0.12 g 1 mmol), purchased from Lancaster Synthesis, in H_2O (20 cm^3) in 1:1, 1:2 or 1:3 stoichiometric ratios, at a variety of temperatures (25–100°C). In each case a pale yellow precipitate (**I**) formed (instantaneously <30°C or for 1:3 ratio) with the empirical formula $UC_{18}H_{18}N_3O_{10.5}$.

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Table 1
Crystallographic data

Empirical Formula	$C_{24}H_{24}N_6O_{24}U_3$
M_r	1494.57
Crystal system; space group	triclinic; P1 (#2)
Colour; habit	yellow; prismatic
Dimensions	0.07×0.17×0.20
a; b; c (Å)	8.841(2); 13.595(4); 8.402(2)
α; β; γ (°)	101.15(2); 101.80(2); 108.00(2)
Cell volume (Å^3); density calculated (g cm^{-3})	928 (1); 2.674
F(000); No. of reflections	678; 25
2θ range (°); temperature (°C)	28.6–37.5; 21
Attenuators (Zr foil factors)	1.1, 1.3, 1.5
Take-off angle (°)	6.0
Detector aperture (mm); crystal to detector (cm)	6.0×6.0; 40
Scan type; scan rate	$\omega/2\pi$; 32.0°/min in ω (2 rescans)
Scan width; $2\theta_{\max}$ (°)	$(1.42+0.30 \tan \theta)°$; 50.1
No. reflections measured	3522 (3289 unique)
Ranges of h, k, l	0 to 10, −16 to 15, −10 to 9
Corrections	Lorentz—polarisation absorption
Structure solution	Direct methods
H-atom treatment	Included in difference map or calculated
Refinement	Full-matrix least-squares
Function minimised; Least-square weights	$\Sigma w(F_o-F_c)^2$; $4F_o^2/\sigma^2(F_o^2)$
p-factor	0.01
Anomolos dispersion	All non-H atoms
No. variables; observations [$I>3\sigma(I)$]	259; 2498
Reflection/parameter ratio; goodness of fit	9.64; 1.65
Residuals: R; R_w	0.035; 0.033
Max shift/error final	<0.01
Max; min peaks in final diff. map	1.78 e$^-$ Å^{-3}; −2.08 e$^-$ Å^{-3}

$UO_2(NO_3)_2{\cdot}6H_2O$ (0.5 g 1 mmol) was dissolved in H_2O (20 cm^3) at room temperature and an aqueous solution of Hmpa (0.04 M, 1 cm^3, i.e. <1:1) was added dropwise with stirring. The mixture was then allowed to stand for two weeks to produce yellow prismatic crystals (**II**), which analysed as: $U_3C_{24}H_{24}N_6O_{24}$.

Microanalytical data were provided by a Carlo-Erba 1108 Elemental Analyser (C, H and N) and a Fisons Horizon ICP-OES (U). The TG/DTA spectra were recorded on a Seiko Instruments SSC/5200 TG/DTA220 Analyser. IR data were recorded upon an ATI Mattson Genesis Series FTIR Spectrometer. The solid-state ^{13}C NMR data were recorded by a Varian Unity 300 (75.429 MHz) spectrometer with a 89-mm bore magnet (Oxford Instruments) and 7-mm cross polarising, magic angle spinning broad band probe (Duty Scientific). Crystallographic measurements were made on a Rigaku AFC5R X-ray diffractometer with graphite-monochromated Mo(Kα) radiation and a 12-kW rotating anode generator (Table 1).

3. Results and discussion

The structure of **II** consists of centrosymmetric units containing uranium atoms. Formally, one molecule of dehydrated starting material, in which uranium has a coordination number of 6, is trapped between two $[UO_2(mpa)_2(H_2O)]$ units, both with equatorial coordination numbers of 5, by bridging carboxylates (Fig. 1). H-bonded water molecules terminate the trinuclear chain at each end. Intramolecular bond lengths and angles are given in Table 2. The TG/DTA trace for **II** showed a two stage decomposition (Fig. 2), comprising an endothermic change at 130.6°C and an exothermic change at 465.0°C. Endothermic changes are characteristic of the removal of solvent or molecules of protonated ligand. Given that the final product of decomposition was UO_3, (57.17% of the

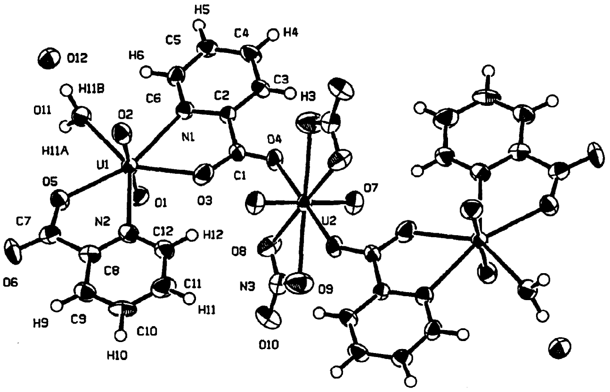

Fig. 1. ORTEP picture of crystal structure of compound **II**.

Table 2
Selected bond angles and lengths for compound **II**

U1-O1	1.739(8)	N2-C12	1.34(1)	O5-U1-O11	78.7(3)
U1-O2	1.748(8)	C1-C2	1.48(1)	O5-U1-N2	64.2(3)
U1-O3	2.330(8)	C2-C3	1.35(1)	O11-U1-N1	77.9(3)
U1-O5	2.348(8)	C3-C4	1.38(2)	O4-U2-O7	87.6(3)
U1-O11	2.360(7)	C4-C5	1.40(1)	O4-U2-O7	92.4(3)
U1-N1	2.59(1)	C5-C6	1.36(2)	O4-U2-O8	66.1(3)
U1-N2	2.57(1)	C7-C8	1.52(2)	O4-U2-O8	113.9(3)
U2-O4	2.403(7)	C8-C9	1.38(2)	O4-U2-O9	116.1(3)
U2-O7	1.756(8)	C9-C10	1.38(2)	O4-U2-O9	63.9(3)
U2-O8	2.526(8)	C10-C11	1.39(2)	O7-U2-O7	180.00
U3-O9	2.500(9)	C11-C12	1.38(2)	O7-U2-O8	89.2(3)
O3-C1	1.29(1)	O11-H11A	0.989	O7-U2-O8′	90.8(3)
O4-C1	1.24(1)	O11-H11B	0.950	O7-U2-O9	89.7(4)
O5-C7	1.28(1)	O1-U1-O2	1.77.8(4)	O7-U2-O9′	90.3(4)
O6-C7	1.22(1)	O1-U1-O3	91.5(3)	O8-U2-O9	50.0(3)
O8-N3	1.27(1)	O1-U1-O5	88.4(3)	O8-U2-O9′	130.0(3)
O9-N3	1.27(1)	O1-U1-O11	92.8(3)	U1-O3-C1	128.4(7)
O10-N3	1.20(1)	O1-U1-N1	86.6(3)	U2-O4-C1	134.4(8)
N1-C2	1.35(1)	O1-U1-N2	92.2(3)	U1-O5-C7	129.1(7)
N1-C6	1.35(1)	O3-U1-N1	63.7(3)		
N2-C8	1.34(1)	O3-U1-N2	76.0(3)		

initial mass present), the empirical molecular mass was calculated as 500 [M_r(**II**)=1494], for the trinuclear species). The first step accounted for 4.80% mass loss ($4H_2O$=4.82%); the second step was a 38.03% mass loss (4mpa+2(NO_3^-)-3[O]=37.75%). The TG/DTA trace for **I** showed a three stage decomposition (Fig. 3), comprising two slightly endothermic changes at 79 and 232°C and a highly exothermic change at 465°C. The shift of the dehydration endotherm from 79°C (**I**) to 130.6°C (**II**) is evidence of the water molecules being more strongly bound in **II**. In **I** they are all present as extrinsic water of crystallisation, whereas in **II** half are directly bonded to uranium centres and half are involved in a strong H-bonding network, linking together the trinuclear units. The empirical molecular mass was calculated to be 648 [M_r(**I**)=650]. The first step in the trace accounted for a 6.90% mass loss ($2.5H_2O$=6.92%); the second step was a 16.33% mass loss (Hmpa=18.92%); the third step was a 32.62% mass loss (2mpa-[O]=35.08%). IR data are shown in Fig. 4 and assignments made in Table 3. NMR data revealed the three different forms of the carboxylate group present in these two products. The spectrum for **II** recorded peaks at 178.9 ppm (tridentate bridging CO_2^-) and 173.9 ppm (bidentate chelating CO_2^-) and the spectrum for **I** recorded peaks at 172.7 ppm (bidentate chelating CO_2^-) and 168.5 ppm (free protonated acid). The observed pattern is as we would predict, with the more deshielded quaternary carbon centre (as a result of increased coordination), having the higher chemical shift in each case. Additional peaks (120–155 ppm) in both spectra were characteristic of the aromatic carbon centres.

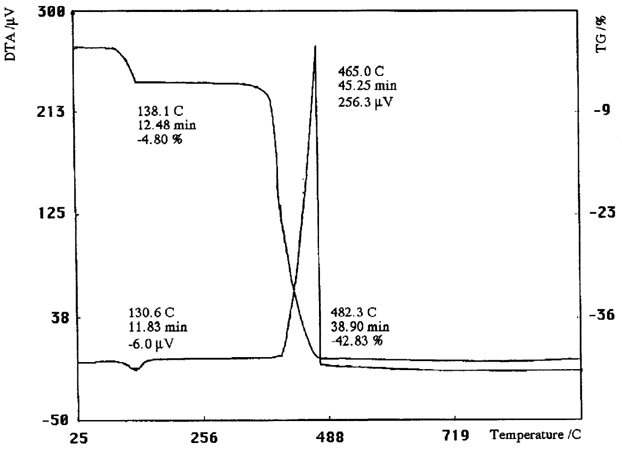

Fig. 2. TG/DTA of compound **II**.

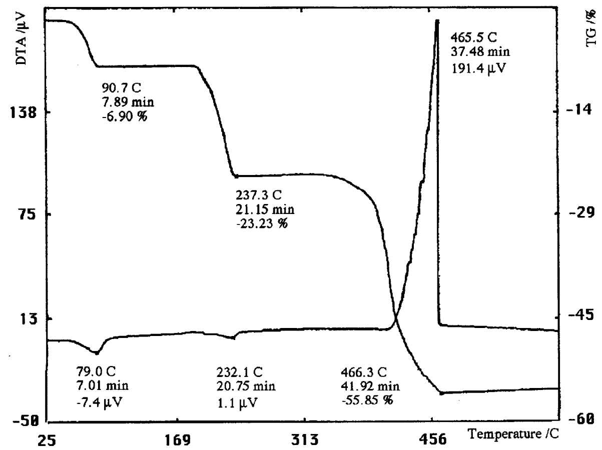

Fig. 3. TG/DTA of compound **I**.

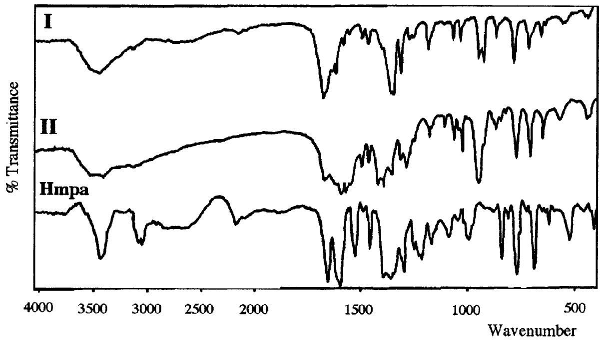

Fig. 4. Infrared data for compounds **I**, **II** and Hmpa.

4. Conclusions

Product **I** [$UO_2(mpa)_2$]·(Hmpa)·$2.5H_2O$ is formed whenever starting stoichiometries of UO_2^{2+} to Hmpa of 1:1, 1:2 or 1:3 are reacted together, regardless of the temperature of the solution. When the concentration of

Table 3
Infrared assignments for compound **I**, **II** and Hmpa

Compound **I**	Compound **II**	Hmpa proligand
3420 broad (H_2O)	3420 broad (H_2O)	3427 narrow (O-H)
1690 st (CO_2H)	1681 wk (CO_2H)	1654 st (CO_2H)
1585 m (assym CO_2^-)	1583 st (assym CO_2^-)	
	1542 st (NO_3^-)	1536 st (NO_3^-)
	1492 m (NO_3^-)	1490 m (NO_3^-)
1360 st (sym CO_2^-)	1360 st (sym CO_2^-)	1353 st (O-H)
964 st (UO_2^{2+})	960 st (UO_2^{2+})	
939 st (UO_2^{2+})	930 st (UO_2^{2+})	
780 m (C-H) out of pl.	768 m (C-H) out of pl.	768 st (C-H) out of pl.
674 m (C-H) sub. ring	670 m (C-H) sub. ring	688 st (C-H) sub. ring

Hmpa is reduced, such that the ratio falls to 1:0.04, the reaction time is increased and the trinuclear product (**II**), for which crystallographic data is provided, is formed. Following comparisons of the analytical data for the two compounds and solution of the structure of **II**, we can predict an equatorial coordination number of 4 for **I**.

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References

[1] G. Bombieri, G., de Paoli, in: A.J., Freeman, C. Keller (Eds.), Handbook on the Physics and Chemistry of the Actinides, Vol. 3, Elsevier, Amsterdam, 1985, p. 75.
[2] Gmelin Handbuch der Anorganischen Chemie, 8th ed. Suppl Ser Uranium, vol. E1 and E2, Springer, Berlin Heidelberg New York, 1979 and 1980.
[3] J. Leciejewicz, et al., Structure and Bonding 82 (1995) 43.
[4] M.A. Vaidya, et al., Inorg. Chim. Acta. 143 (1988) 123.
[5] M.A. Vaidya, S.C. Jain, Indian J. Chem. 28 (1989) 135.
[6] T.N. Shrivastava, et al., Indian J. Chem. 21A (1982) 309.
[7] N.W. Alcock, R.E. Timms, J. Chem. Soc. A (1968) 1876.
[8] M. Yutaka, O. Rokuro, J. Orgmet. Chem. 10 (1967) 247.
[9] S.G. Deshpande, S.C. Jain, Indian J. Chem. 29A (1990) 1215.
[10] A. Cousson, et al., Acta. Cryst. C47 (1991) 2065.
[11] G.A. Battiston et al. J. Chem. Soc. (Dalton) (1979) 1965.