Inorganica Chimica Acta, 191 (1992) 241–248

f Element croconates
2. Thorium(IV) and dioxo-uranium(VI) croconates – synthesis, crystal structure and thermal behaviour

Chantal Brouca-Cabarrecq and Jean-Christian Trombe*
CEMES-LOE/CNRS, 29 rue Jeanne Marvig, B.P. 4347, 31055 Toulouse Cédex (France)

(Received July 21, 1991)

Abstract

Two complexes of actinide croconates, thorium(IV) and dioxo-uranium(VI) were prepared: $Th(H_2O)_7(C_5O_5)_2$ and $UO_2(H_2O)K_2(C_5O_5)_2$. The crystal structure of these complexes was determined by X-ray single crystal technique. The thorium croconate hydrated crystallizes in the orthorhombic system, space group *Pnma*. It is made of discrete, neutral entities. In this complex the croconate ligand is only monodentate. The uranyl hydrated potassium croconate crystallizes in the monoclinic system, space group *C2/c*. This complex has a 3D structure presenting tunnels in which are localized the water molecules bound to the uranium atom. The outstanding feature of this structure is the high number (seven) of metals bound to each croconate ligand. This latter is bis-monodentate towards the uranium atom, bis-chelating towards the potassium atom and the two oxygen atoms are bound to one supplementary potassium atom. The thermal behaviour of these complexes was studied. For the thorium croconate hydrated dehydration occurs first, followed by the decomposition of the croconate ligand which yields thorium oxide, ThO_2. A more complex and interesting behaviour is noticed for the complex $UO_2(H_2O)K_2(C_5O_5)_2$. The products formed at the outset of the decomposition seem to influence the further stages.

Introduction

A systematic study of lanthanide(III) croconates [1] has been developed in previous articles [1–3]. Lanthanide croconates appear to be very sensitive to the presence of alkaline elements. By reacting on a potassium or sodium croconate, lanthanide elements yield two phases: the first one containing only the lanthanide, the other one containing both elements, lanthanide and alkaline [2]. Lanthanide croconates free from alkaline elements are prepared by using croconic acid or triethanol-ammonium croconate. Two families are observed: **1**-Ln with Ln(III) = Ce, Pr, Nd, Sm, Eu, Gd and **2**-Ln with Ln(III) = Tb, Dy, Ho, Er, Yb [1]. Some lanthanides, lanthanum, lutetium and yttrium, fail to give croconate in the conditions generally used for this kind of preparation (evaporation in an open system in the presence of daylight); they require special conditions.

In the literature the croconate ligand exhibits either 1,2,4-coordination(1,2-chelation) [4, 5] or 1,2-chelation [6–9]. In lanthanide croconates, this ligand displays several coordination modes: chelating or bis-chelating for the family **1**-Ln, monodentate or trans-monodentate for the family **2**-Ln.

For comparison with the lanthanide croconates, the present paper deals with some actinide ones, namely thorium(IV) and dioxo-uranium(VI). The conditions of synthesis as well as the crystal structure and thermal analysis are presented.

Experimental

The croconate ligand was used under three forms: the synthesis of potassium croconate is described in ref. 10, the synthesis of triethanol-ammonium croconate and croconic acid in ref. 1.

$Th(H_2O)_7(C_5O_5)_2$ (1)

0.25 mmol of thorium nitrate was added to 0.5 mmol of croconate ligand in 25 ml of water under stirring. After a few minutes an orange precipitate appeared in the solution and was filtered off, then washed with water and air dried. In order to enhance the crystal growth, the initial solution was set at 4 °C in a refrigerator. After two weeks, crystals suitable for structural determination appeared. Whatever the counterion associated with the croconate (K^+, H^+, $(CH_3CH_2OH)_3NH^+$)), the precipitate and the crystal presented the same X-ray powder pattern. Elemental

---

*Author to whom correspondence should be addressed.

0020-1693/92/$5.00

analysis was consistent with the formula deduced from structural determination, $Th(H_2O)_7(C_5O_5)_2$. Found: Th, 37.4; C, 18.5; H, 2.1. Calc.: Th, 36.36; C, 18.81; H, 2.19%.

$UO_2(H_2O)K_2(C_5O_5)_2$ (2)

For the uranyl ion only potassium croconate gave a crystallized compound; croconic acid or triethanol-ammonium yielded a glassy product. 0.25 mmol of uranyl acetate in 10 ml of water was added to 0.5 mmol of potassium croconate in 15 ml of water. Upon evaporation purple crystals were obtained. Elemental analysis agreed well with the formula deduced from the structural determination: $UO_2(H_2O)K_2(C_5O_5)_2$. Found: U, 37.4; K, 12.0; C, 18.2; H, 0.5. Calc.: U, 36.83; K, 12.10, C, 18.57; H, 0.31%.

The techniques used for this study, either in the crystal structure determination or in the thermal analysis, were described in ref. 1.

Crystal structure determination

Crystal data and conditions of intensity measurements are given in Table 1. For both the complexes, absorption corrections were applied to the intensity data [12].

$Th(H_2O)_7(C_5O_5)_2$

Thorium croconate crystallizes in an orthorhombic system with $a = 8.245(2)$, $b = 16.329(1)$, $c = 12.373(2)$ Å. Systematic absences of reflections $0kl$ with $k+l=2n+1$, $hk0$ with $h=2n+1$ are compatible with the space groups *Pnma* (centrosymmetric) and $Pn2_1a$ (non-centrosymmetric). The structure was successfully carried out using the centrosymmetric group.

The thorium atom occupied special positions on the mirror (4c) as well as some oxygen atoms of water molecules (Ow1, Ow2, Ow4). One croconate cycle and two supplementary water molecules were located. The hydrogen atoms of all the water molecules could be found from difference Fourier map; they were introduced as a fixed contributor. All the other atoms were refined anisotropically. In the last cycle of refinement the largest (variable shift)/(e.s.d.) ratio was 0.07 and the reliability factors converged at $R = 0.021$, $R_w = 0.029$ for 141 variables and 1928 observations ($I > 3\sigma(I)$). The error in an observation of unit weight was 1.07 e^-. The final parameters and their e.s.d.s are given in Table 2.

$UO_2(H_2O)K_2(C_5O_5)_2$

A monoclinic system with $a = 14.565(2)$, $b = 7.964(1)$, $c = 12.911(3)$ Å, $\beta = 109.28(1)°$ is found for the uranyl dipotassium croconate. Systematic absences of reflections hkl with $h+k=2n+1$, $h0l$ with h, $l=2n+1$ are consistent with space groups *C2/c* (centrosymmetric) and *Cc* (non-centrosymmetric). The structure was refined using the centrosymmetric group.

The heavy atom, uranium, was localized by the Patterson technique; the other atoms appeared by using the difference Fourier map. Two atoms occupied special positions along the twofold axis (4e): uranium and the oxygen atom of the water molecule Ow1. It was possible to find the position of the hydrogen atom bound to the water molecule Ow1. The hydrogen atom was introduced as a fixed contributor, the other atoms were refined with an anisotropic temperature factor. Resulting reliability factors were equal to $R = 0.038$ and $R_w = 0.047$ for 1776 observations with $I > 3\sigma(I)$ and 120 variables; the largest (variable shift)/(e.s.d.) was equal to 0.02. The error in an observation of unit weight was 1.06 e^-. The final difference Fourier map did not give significant features. The atomic coordinates and the equivalent or isotropic thermal parameters with their standard deviations are given in Table 3.

Description and discussion of the structure

$Th(H_2O)_7(C_5O_5)_2$

The structure is made of discrete, neutral, mononuclear and symmetrical entities (Fig. 1). The mirrors parallel to the plane (010) containing the thorium atom and three water molecules are the element of symmetry of such entities. From side to side of these mirrors are found croconate ligands and two water molecules. Hydrogen bonding or van der Waals interactions between oxygen atoms and water molecules plays a noticeable role in the cohesion of these entities (Table 4).

The thorium atom is bound to nine oxygen atoms; the thorium–oxygen distances have an average value of 2.458(4) Å. The largest Th–O distance corresponds to the water molecule Ow4 (2.571(5) Å) while the smallest one corresponds to the croconate oxygen atom O1 (2.371(3) Å) (Table 4). The polyhedron of coordination is closed to a monocapped square antiprism; the dihedral angle between the two bases (Ow1, Ow2, Ow3, Ow3^i) and (Ow5, Ow5^i, O1, O1^i) is equal to 2.24°. The apical position of the square antiprism is occupied by Ow4 (Fig. 2).

The croconate ligand is monodentate: such a coordination scheme was met for the lanthanide family **2**-Ln [1]. The lenghtening of the distance C1–O1 (1.265(4) versus 1.243(5) Å (average)) results in the shortening of the distances C1–C2 and C1–C5 with respect to the other C–C distances (Table 4).

The croconate anion is not strictly planar; atom to mean plane distances reach 0.089(4) Å (O4). Hydrogen bonding could account for this non-planarity: except for the O1 atom, all croconate oxygen atoms are engaged

TABLE 1. Experimental crystallographic data for $Th(H_2O)_7(C_5O_5)_2$ and $UO_2(H_2O)K_2(C_5O_5)_2$

	$Th(H_2O)_7(C_5O_5)_2$	$UO_2(H_2O)K_2(C_5O_5)_2$
Crystal data		
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	*C2/c*
a (Å)	8.245(2)	14.565(2)
b (Å)	16.329(1)	7.964(1)
c (Å)	12.373(2)	12.911(3)
β		109.28(1)
V (Å^3)	1666.0(5)	1414(7)
Z	4	4
Molecular weight (g)	638.04	646.23
ρ_{calc} (g/cm^3)	2.545	3.037
μ (Mo Kα) (cm^{-1})	93.53	115.53
Morphology	parallelipiped	parallelipiped
Dimension (mm)	0.4×0.07×0.1	0.15×0.10×0.10
Transmission coefficient: min., max.	82.6, 99.6	72.70, 99.91
Data collection		
Temperature (K)	293	293
Wavelength (Mo Kα) (Å)	0.71073	0.71073
Monochromator	graphite	graphite
Scan mode	ω–2θ	ω–2θ
Scan width (°)	0.75+0.35 tgθ	0.85+0.35 tgθ
Take-off angle (°)	3.5	3
Max. Bragg angle (°)	30	30
Scan speed[a]		
SIGPRE[a]	0.75	0.80
SIGMA[a]	0.018	0.018
VPRE (°/min)[a]	10	7
T_{max} (s)[a]	70	90
Intensity control reflections (every 3600 s)	0 0 8/3 1 3/0 5 5	8 0 −6/5 1 −5/−2 2 3
Orientation control reflections (every 100 reflections)	6 0 0/0 0 14/2 10 7	10 0 0/0 0 10/0 6 1
Attenuation factor	19.4	19.4
Structure refinement		
Reflections collected	2773	2285
Reflections used	1928 ($I > 3\sigma(I)$)	1776 ($I > 3\sigma(I)$)
No. refined parameters	141	120
Weighting, w^{-1}	$\sigma^2(F_o) + (0.02F_o)^2$	$\sigma^2(F_o) + (0.015F_o)^2 + 0.4$
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.021	0.038
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w F_o^2]^{1/2}$	0.029	0.047

[a] For definition of parameters see ref. 11.

in this kind of bonding (Table 4). O4 atom is submitted to two forces in the same direction almost perpendicular to the croconate plane Ow2–H1w2–O4^{iii} and Ow4–H1w4–O4^{v} (Table 4).

There are four $Th(H_2O)_7(C_5O_5)_2$ entities per unit cell. The crystal structure is ensured by hydrogen bonds, already mentioned, and by stacking of croconate planes related by an inversion center. A projection on to the mean plane of the croconate shows an overlap at the level of the C1, C2, C3, O3 atoms (Fig. 3). Distances of these atoms to the mean plane of the facing croconate range between 3.278(4) and 3.310(4) Å. Such distances between the π system might agree with van der Waals interactions [13].

$UO_2(H_2O)K_2(C_5O_5)_2$

There are four units of formula $UO_2(H_2O)K_2(C_5O_5)_2$ per C-centered unit cell. A view of a projection of the crystal structure onto the plane (010) is given in Fig. 4.

The uranium atom located on a twofold axis is bound to four oxygen atoms (O11, O11^{i}, O21^{ii}, O21^{iii}) of four different (but not crystallographically independent) croconate ligands: there is one croconate per assymmetric cell. From this croconate position the set of four cro-

TABLE 2. Atomic positions and equivalent thermal parameters for $Th(H_2O)_7(C_5O_5)_2$

Atom	x	y	z	B (Å^2)^a
Th	0.09732(2)	1/4	0.04881(2)	1.452(3)
Ow1	0.0708(5)	1/4	0.2420(4)	2.63(8)
Ow2	−0.1899(5)	1/4	−0.073(4)	2.47(8)
Ow3	−0.0562(3)	0.3734(2)	0.1085(3)	2.33(5)
Ow4	0.3432(5)	1/4	−0.0788(4)	2.63(8)
Ow5	0.0635(3)	0.3466(2)	−0.1046(3)	2.62(5)
O1	0.2805(3)	0.1464(2)	0.1050(2)	2.20(5)
O2	0.6236(3)	0.1174(2)	0.1447(3)	2.87(6)
O3	0.6784(4)	−0.0582(2)	0.1523(3)	3.70(6)
O4	0.3699(4)	−0.1406(2)	0.1170(3)	3.97(7)
O5	0.1157(3)	−0.0136(2)	0.1020(3)	2.57(5)
C1	0.3453(4)	0.0769(2)	0.1182(3)	1.57(6)
C2	0.5170(4)	0.0639(2)	0.1368(3)	1.83(6)
C3	0.5461(5)	−0.0249(2)	0.1407(3)	2.02(6)
C4	0.3889(4)	−0.0661(2)	0.1239(3)	2.15(6)
C5	0.2646(4)	−0.0019(2)	0.1142(3)	1.83(6)
H11	0.089	0.199	0.278	4.0*
H12	−0.244	0.200	−0.040	4.0*
H13	−0.011	0.429	0.108	4.0*
H23	−0.168	0.383	0.131	4.0*
H14	0.419	0.203	−0.089	4.0*
H15	−0.004	0.395	−0.117	4.0*
H25	0.125	0.350	−0.173	4.0*

[a] Starred items: atoms were refined with isotropic thermal parameters.

TABLE 3. Atomic positions and equivalent thermal parameters for $UO_2(H_2O)K_2(C_5O_5)_2$

Atom	x	y	z	B (Å^2)
U	1/2	0.62575(5)	1/4	1.207(5)
K	0.6984(1)	0.3308(3)	0.1509(2)	2.61(3)
Ow(1)	1/2	0.927(1)	1/4	4.2(2)
O(1)	0.3729(4)	0.6300(8)	0.2238(5)	2.1(1)
O(11)	0.4966(4)	0.3934(8)	0.1339(5)	2.1(1)
O(21)	0.5169(4)	0.2747(8)	−0.0694(4)	1.9(1)
O(31)	0.3763(5)	−0.0044(9)	−0.1505(5)	2.9(1)
O(41)	0.2721(5)	−0.0507(9)	0.0020(5)	2.8(1)
O(51)	0.3234(5)	0.227(1)	0.1608(5)	2.9(1)
C(11)	0.4425(6)	0.284(1)	0.0720(6)	1.6(1)
C(21)	0.4545(5)	0.223(1)	−0.0272(6)	1.5(1)
C(31)	0.3869(6)	0.085(1)	−0.0689(6)	1.7(1)
C(41)	0.3303(6)	0.062(1)	0.0069(6)	1.8(1)
C(51)	0.3599(5)	0.198(1)	0.0904(6)	1.8(1)
H	0.458	0.983	0.282	4.0^a

[a] The corresponding atom was refined with isotropic thermal parameters.

conates is obtained by application of the twofold axis and by inversion centers (½, ½, 0; ½, ½, ½). Thus infinite chains $[UO_2(H_2O)(C_5O_5)_2{}^{2-}]_\infty$ are formed. This chain is reproduced by the other symmetry elements of the cell (e.g. twofold screw axis). The tridimensional feature of this structure is assumed by the potassium ion.

In addition to four croconate oxygen atoms the uranium atom is bound to one water molecule (Ow1) and to two uranyl oxygen atoms: the presence of these latter atoms is characterized by short U–O bonds [14] (Table 5). Except for the uranyl group the other distances U–O are homogeneous enough (Table 5). The coordination polyhedron can be represented as a pentagonal bipyramid (Fig. 5). Such a shape frequently occurs for the uranyl group [15, 16]. The equatorial bonds are longer than the axial ones (Table 5). The uranium atom and its five neighbouring equatorial atoms (O11, O11^{i}, O21^{ii}, O21^{iii} Ow1) are approximately planar: the atom to mean plane distance reaches 0.073(6) Å for O11 and O11^{i}. The angle between this plane and the uranyl bond is equal to 90°.

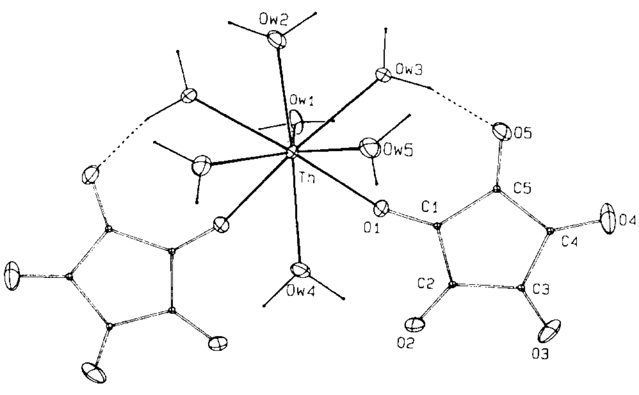

Fig. 1. View of the mononuclear entity of $Th(H_2O)_7(C_5O_5)_2$.

The potassium atom is bound to nine oxygen atoms. The extreme dispersion of the potassium–oxygen distances, between 2.684(7) and 3.238(7) Å, can account for the difficulty to fix a definite coordination polyhedron (Table 5).

The salient feature of this structure is the great number (seven) of metallic atoms related by one croconate ligand. As far as we are aware, this number has never been reached in the croconate structural chemistry. For the lanthanide squarate prepared in close system (pseudo-hydrothermal synthesis) a value of six metal ions had been obtained [17]. The croconate ligand is bis-monodentate towards the uranium atom but it is also bis-chelating towards the potassium atom (Fig. 6). Besides, with the exception of the O51 atom each croconate oxygen atom is coordinated to two metal centers. O31 and O41 are bound to two potassium ions resulting in chains ... K–O31–K–O31 ... or double bridges

$$\mathrm{O41}\underset{\mathrm{K}}{\overset{\mathrm{K}}{\;}}\mathrm{O41}$$

where the K–K distances are equal to 4.705 and 4.789 Å, respectively.

Chelation is the usual mode of coordination for the croconate ligand [4–9]; the case of lanthanide croconate, 1-Ln, is the first occurrence of bis-chelation [1]. Δ is the difference of M–O distances inside the bite. Che-

TABLE 4. Interatomic distances (Å)[a] and bond angles (°) in $Th(H_2O)_7(C_5O_5)_2$

Around Th			
Th–Ow1	2.393(5)		
Th–Ow2	2.462(5)		
Th–Ow3	2.493(3)		
Th–Ow3^{i}	2.493(3)		
Th–Ow4	2.571(5)		
Th–Ow5	2.484(3)		
Th–Ow5^{i}	2.484(3)		
Th–O1	2.371(3)		
Th–O1^{i}	2.371(3)		
Croconate ligand			
C1–C2	1.451(5)	O1–C1–C2	124.5(3)
C2–C3	1.470(5)	O1–C1–C5	126.7(3)
C3–C4	1.475(6)	C5–C1–C2	108.8(3)
C4–C5	1.474(5)	O2–C2–C3	125.2(3)
C5–C1	1.450(5)	O2–C2–C1	126.7(3)
C1–O1	1.265(4)	C1–C2–C3	108.0(3)
C2–O2	1.245(5)	O3–C3–C2	125.7(4)
C3–O3	1.229(5)	O3–C3–C4	126.4(4)
C4–O4	1.224(5)	C2–C3–C4	107.8(3)
C5–O5	1.251(5)	O4–C4–C3	125.2(4)
		O4–C4–C5	127.6(4)
		C3–C4–C5	107.2(3)
		O5–C5–C1	126.0(3)
		O5–C5–C4	125.8(3)
		C1–C5–C4	108.1(3)
Hydrogen bonds and van der Waals contacts			
Intramolecular			
Ow3–O5	2.692(4)	Ow3–H1w3–O5	164.6(2)
Ow1–Ow3	2.806(5)		
Ow2–Ow3	2.704(5)		
Ow3–O1	2.796(4)		
Intermolecular			
Ow1–O2^{ii}	2.619(4)	Ow1–H1w1–O2^{ii}	172.9(3)
Ow2–O4^{iii}	2.696(5)	Ow2–H1w2–O4^{iii}	161.5(3)
Ow3–O2^{iv}	2.680(4)	Ow3–H2w3–O2^{iv}	165.7(2)
Ow4–O4^{v}	3.002(5)	Ow4–H1w4–O4^{v}	159.3(2)
Ow5–O5^{vi}	2.723(4)	Ow5–H1w5–O5^{vi}	164.5(2)
Ow5–O3^{vii}	2.699(4)	Ow5–H2w5–O3^{vii}	108.0(2)

[a] Code of equivalent positions: ^{i}: $x, \frac{1}{2}-y, z$; ^{ii}: $x-\frac{1}{2}, y, \frac{1}{2}-z$; ^{iii}: $-x, -y, -z$; ^{iv}: $x-1, \frac{1}{2}-y, z$; ^{v}: $1-x, -y, -z$; ^{vi}: $-x, y+\frac{1}{2}, -z$; ^{vii}: $1-x, y+\frac{1}{2}, -z$.

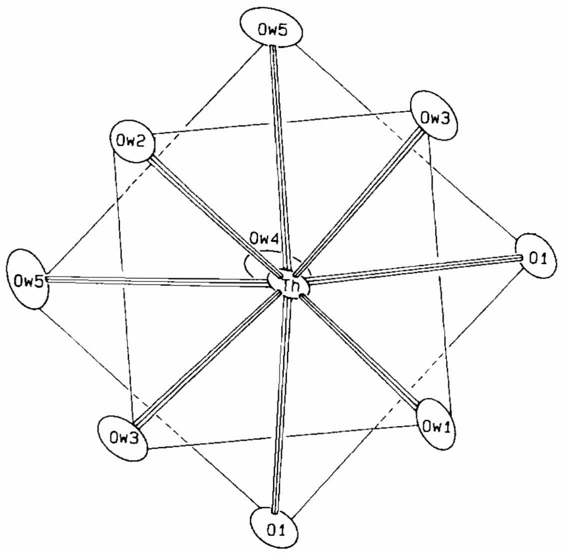

Fig. 2. Monocapped square antiprism around thorium atom.

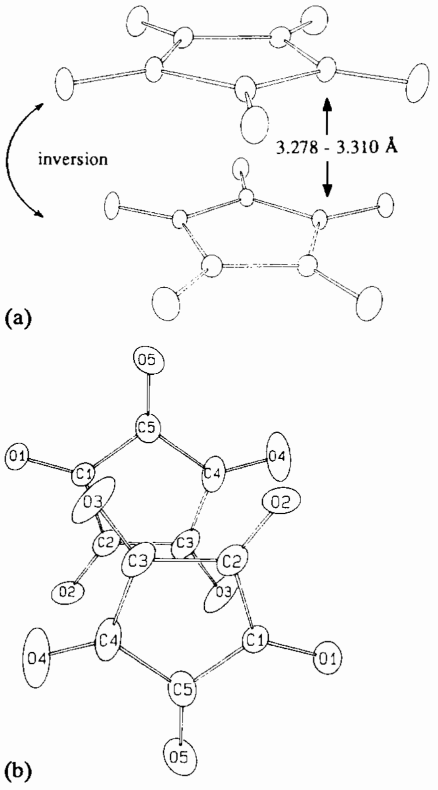

Fig. 3. The stacking of two croconate anions related by an inversion center: (a) side view, (b) projection on to the mean plane of the croconate.

lation is more or less disymmetrical: Δ ranges from 0.004 to 0.34 [4–9]. For lanthanide croconates, 1-Ln, bis-chelation is symmetrical enough (Δ = 0.034 Å) [1] while for this structure it appears to be more disymmetrical, Δ = 0.295 and 0.284 Å for the bites O11–O21 and O31–O41, respectively (Table 5) (Fig. 6).

The effects of chelation or bis-chelation are almost compensated by the strains due to the great number of metallic centers affecting this croconate anion. However oxygen–oxygen distances inside the bite are always smaller than outside (2.88(1) or 2.897(9) Å versus 2.93(1) Å (average)) (Fig. 6). Bond lengths C11–O11 or C21–O21 appear to be longer than the other C–O distances (Table 5). The lengthening of such distances results in the shortening of the C11–C21 distance and thereby the inner angles C51–C11–C21 or C11–C21–C31 are more open than the others. The direction of the forces exerted at the O31 atom by the two potassium ions leads this atom to draw nearer to the O41 atom;

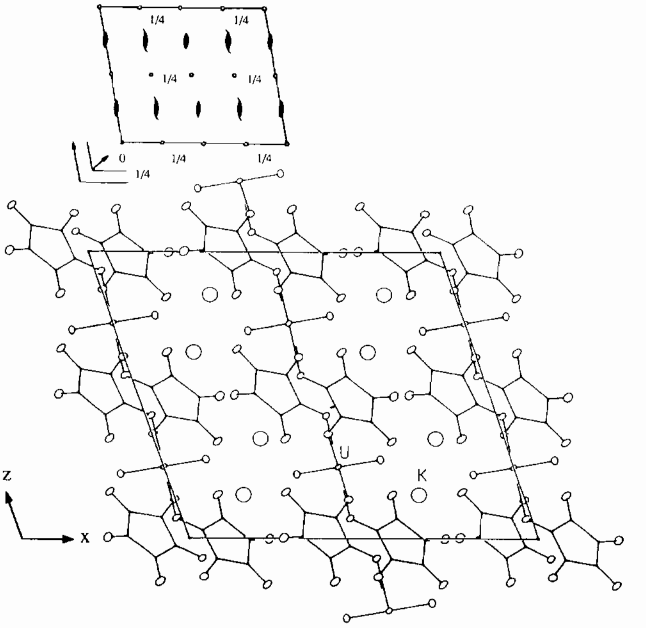

Fig. 4. Projection on to the mean plane (010) of the complex $UO_2(H_2O)K_2(C_5O_5)_2$. Schematic view of the chains $[UO_2(H_2O)(C_5O_5)_2^{2-}]_\infty$ parallel to the plane (100). Water molecules, Ow1, do not appear in this projection because they are located straight above uranium atoms. Bonds between potassium atoms and oxygen atoms are not represented.

this fact strengthens the chelation effects: O31–C31–C21 and O31–C31–C41 are quite different (Fig. 6) (Table 5).

The five carbon atoms are almost coplanar (maximum deviation from planarity is equal to 0.038(8) Å) but if the whole ligand is considered atom to mean plane distances reach 0.170(7) Å (O51).

Although this structure is very compact at the level of the croconate ligand bound to seven metallic centers, it accommodates tunnels in which are localized the water molecules Ow1. These tunnels are parallel to the direction [001]; there are two tunnels per unit cell (Fig. 7). A hydrogen bond occurs between Ow1 and O31$^{\rm iii}$ atoms, a van der Waals contact occurs between Ow1 and O21 atoms. Such effects strenghten the cohesion of the lattice.

Thermal behaviour

The thermogravimetric analysis (TGA) curve for thorium croconate presents two steps (Fig. 8). First, the complex loses the seven water molecules coordinated to the metal atom in a single step process between 150 and 185 °C. This dehydration is endothermic (Fig. 9).

TABLE 5. Interatomic distances (Å)[a] and bond angles (°) in $UO_2(H_2O)K_2(C_5O_5)_2$

Around U		Around K	
U–Ow(1)	2.40(1)	K–O(1)$^{\rm iv}$	2.886(6)
U–O(1)	1.768(5)	K–O(1)$^{\rm i}$	3.238(7)
U–O(1)$^{\rm i}$	1.768(5)	K–O(11)	2.917(7)
U–O(11)	2.371(6)	K–O(21)	3.212(5)
U–O(11)$^{\rm i}$	2.371(6)	K–O(31)$^{\rm v}$	2.817(7)
U–O(21)$^{\rm ii}$	2.397(6)	K–O(31)$^{\rm vi}$	3.288(6)
U–O(21)$^{\rm iii}$	2.397(6)	K–O(41)$^{\rm v}$	3.101(8)
		K–O(51)$^{\rm i}$	2.684(7)
Croconate ligand			
C(11)–C(21)	1.43(1)	O(21)–C(21)–C(11)	125.8(7)
C(21)–C(31)	1.45(1)	C(11)–C(21)–C(31)	108.8(7)
C(31)–C(41)	1.48(1)	O(31)–C(31)–C(21)	128.9(8)
C(41)–C(51)	1.49(1)	O(31)–C(31)–C(41)	123.2(7)
C(51)–C(11)	1.47(1)	C(21)–C(31)–C(41)	107.8(7)
C(11)–O(11)	1.264(9)	O(41)–C(41)–C(31)	125.7(8)
C(21)–O(21)	1.27(1)	O(41)–C(41)–C(51)	127.0(8)
C(31)–O(31)	1.24(1)	C(31)–C(41)–C(51)	107.2(7)
C(41)–O(41)	1.22(1)	O(51)–C(51)–C(11)	127.8(7)
C(51)–O(51)	1.22(1)	O(51)–C(51)–C(41)	125.9(8)
O(11)–C(11)–C(21)	124.5(8)	C(11)–C(51)–C(41)	106.3(7)
O(11)–C(11)–C(51)	126.2(8)		
C(51)–C(11)–C(21)	109.3(6)		
O(21)–C(21)–C(31)	125.4(7)		
Hydrogen bonds and van der Waals contacts			
Ow1–O31$^{\rm iii}$	2.608(8)	Ow1–H–O31$^{\rm iii}$	157.7(6)
Ow1–O(21)$^{\rm iii}$	2.775(8)		
Ow1–O(21)$^{\rm ii}$	2.775(8)		
O(11)–O(21)$^{\rm ii}$	2.759(8)		

[a] Code of equivalent positions: $^{\rm i}$: $1-x, y, \frac{1}{2}-z$; $^{\rm ii}$: $1-x, 1-y, -z$; $^{\rm iii}$: $x, 1-y, \frac{1}{2}+z$; $^{\rm iv}$: $x+\frac{1}{2}, y-\frac{1}{2}, z$; $^{\rm v}$: $1-x, -y, -z$; $^{\rm vi}$: $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $^{\rm vii}$: $\frac{1}{2}+x, \frac{1}{2}+y, z$.

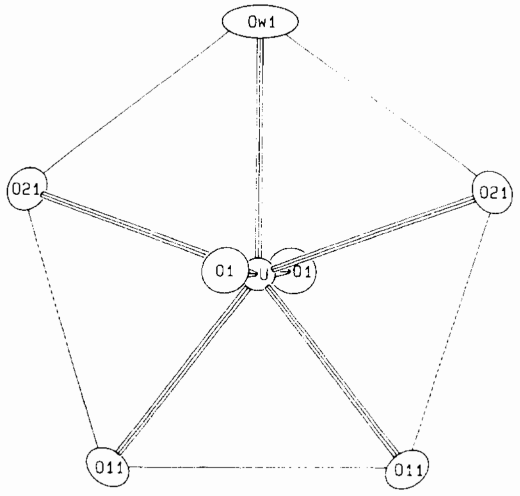

Fig. 5. Pentagonal bipyramid around uranium atom.

The second step corresponds to the croconate ligand decomposition and gives rise to the formation of thorium(IV) oxide, ThO_2. It takes place in a narrow temperature range between 280 and 330 °C (eqn. (1)). This process begins slowly and as the temperature becomes higher and higher a steep slope is observed. In the conditions used (He/O_2) the reaction is exoth-

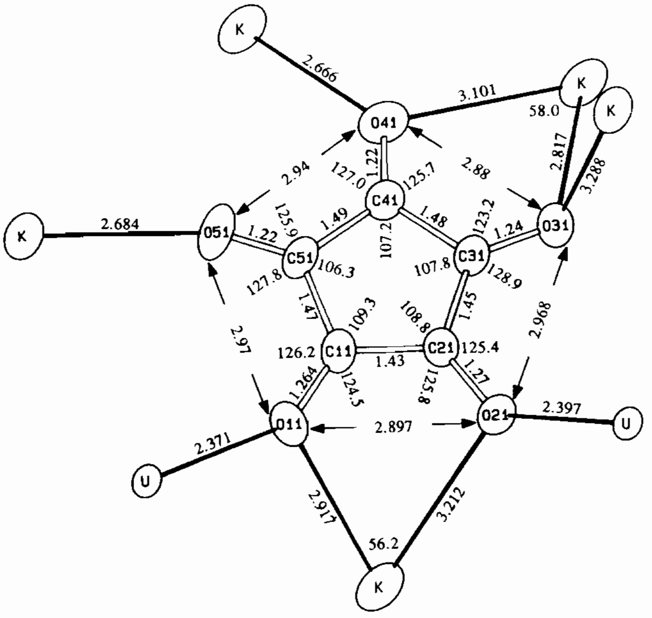

Fig. 6. The coordination mode of the croconate anion.

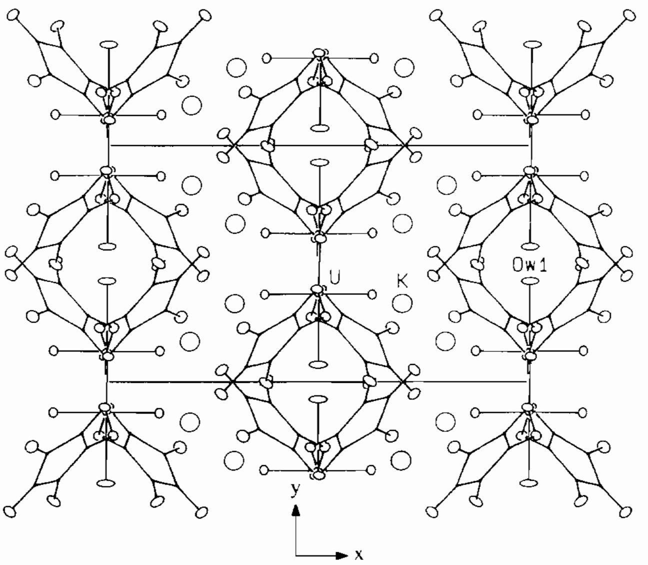

Fig. 7. Projection on to the plane (001) of the complex $UO_2(H_2O)K_2(C_5O_5)_2$. Tunnels parallel to the direction [001] appear. Bonds between potassium atoms and oxygen atoms are not represented.

ermic: two exothermic peaks are noticed, the minor corresponds to the beginning of the decomposition, and the major to the fast decomposition (Fig. 9).

$$Th(H_2O)_7(C_5O_5)_2 \xrightarrow[\Delta m_1]{\substack{150\text{–}185\ ^\circ C \\ He\text{–}O_2}} Th(C_5O_5)_2$$

$$+7\overset{\nearrow}{H_2O} \xrightarrow[\Delta m_2]{\substack{280\text{–}330\ ^\circ C \\ He+O_2}} ThO_2+10C\overset{\nearrow}{O_2} \qquad (1)$$

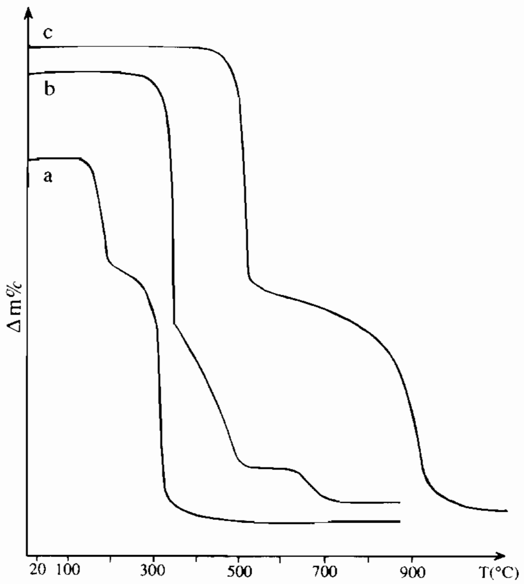

Fig. 8. TGA curves for $Th(H_2O)_7(C_5O_5)_2$ (a), $UO_2(H_2O)K_2(C_5O_5)_2$ (b), $K_2(C_5O_5)$ (c).

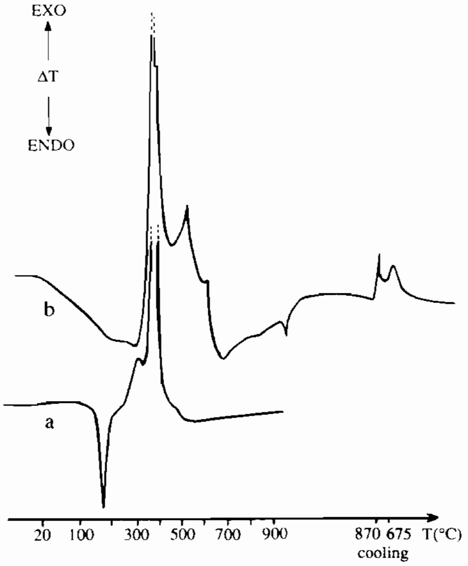

Fig. 9. TDA curves for: $Th(H_2O)_7(C_5O_5)_2$ (a), $UO_2(H_2O)K_2(C_5O_5)_2$ (b).

Obs.: $\Delta m_1 = 19.0$, $\Delta m_2 = 24.2$.
Calc.: $\Delta m_1 = 19.75$, $\Delta m_2 = 21.98$.

For potassium uranyl croconate, the TGA curve is at least a three step process (Fig. 8). Decomposition starts at about 285 °C and rapidly reaches a point at 345 °C, then a second stage of slow decomposition takes place till 515 °C where a quasi horizontal level is observed. Between 285 and 345 °C weight loss is compatible with dehydration and one (upon two) croconate decomposition to lead in the solid phase to

UO_3 and $K_2C_5O_5$ (eqn. (2)). The water molecule of the initial complex is strongly bound to the lattice, since its departure is observed at high temperature. In fact no endotherm is clearly shown but perhaps it is overlapped by the strong exotherm at about 350 °C corresponding to the croconate decomposition (Fig. 9). The solid compound at 345 °C is amorphous, however its IR spectrum exhibits croconate bonds.

Beyond 345 and upto 515 °C, weight loss data indicate both the decomposition of the second croconate to give potassium carbonate and the concomitant decarbonatation of half the potassium carbonate which reacts over the uranium trioxide to yield $\frac{1}{2}K_2U_2O_7$ (eqn. (2), Fig. 8). One broad exothermic peak centered at about 500 °C appears in the TDA curve (Fig. 9). After a heating at about 515 °C and a cooling down, the nature of the solid product can be precised: a mixed oxide, $K_2U_2O_7$, appears on its X-ray powder pattern [18], and carbonate bands are visible on its IR spectrum, indicating the presence of potassium carbonate.

The third weight loss occurring between 640 and 700 °C corresponds to the decarbonation of the remaining potassium carbonate. In the TDA curve, one broad endothermic peak is noticed in this temperature range, however further peaks (endothermic or exothermic) occur on heating more or on cooling (Fig. 9). The final product at ambient temperature appears to consist of a uranium oxide, $K_2U_2O_7$, and potassium oxide, according to its X-ray powder pattern.

At least two questions are worth discussing by comparison with the thermal behaviour of the potassium croconate only. Croconate decomposition of the potassium croconate is observed between 490 and 515 °C to give potassium carbonate; the decarbonation of this latter phase occurs very slowly between 850 and 900 °C (Fig. 8, curve c). For the uranyl potassium croconate these temperatures are lower. The uranium trioxide formed at 345 °C hastens the decomposition of potassium croconate resulting in the formation of K_2CO_3 and a mixed oxide, $K_2U_2O_7$ (Fig. 8, curve b). In a similar way, the latter oxide, can lower the decarbonation of the potassium carbonate to give a new mixed oxide. Such an oxide, K_2UO_4, exists [19] but the final product, when heated at about 900 °C in the conditions used for the thermal analyses (described in ref. 1), reveals only the presence of $K_2U_2O_7$ and potassium oxide. Two exothermic peaks (870 and 675 °C) were noticed when cooling down for the TDA curve (Fig. 9). The appearance of these peaks suggests phase transformation, and perhaps in the conditions used, the oxide K_2UO_4 is unstable.

$$
\begin{aligned}
&UO_2(H_2O)K_2(C_5O_5)_2 \xrightarrow[\Delta m_1]{\substack{285\text{–}345\ °C\\ He\text{–}O_2}} \\
&UO_3 + K_2C_5O_5 + \overset{\nearrow}{H_2O} + 5\overset{\nearrow}{CO_2} \xrightarrow[\Delta m_2]{\substack{345\text{–}515\ °C\\ He\text{–}O_2}} \\
&\tfrac{1}{2}U_2K_2O_7 + \tfrac{1}{2}K_2CO_3 + \tfrac{9}{2}\overset{\nearrow}{CO_2} \xrightarrow[\Delta m_3]{640\text{–}700\ °C} \\
&K_2UO_4 + \tfrac{1}{2}\overset{\nearrow}{CO_2} \xrightarrow{\text{cooling}} \tfrac{1}{2}K_2O + \tfrac{1}{2}U_2K_2O_7 \qquad (2)
\end{aligned}
$$

Obs.: $\Delta m_1 = 39.4$, $\Delta m_2 = 13.7$, $\Delta m_3 = 3.2$.
Calc: $\Delta m_1 = 38.87$, $\Delta m_2 = 15.79$, $\Delta m_3 = 3.4$.

References

1 C. Brouca-Cabarrecq and J.-C. Trombe, *Inorg. Chim. Acta, 191* (1992) 227.
2 J.-C. Trombe and C. Brouca-Cabarrecq, *C. R. Acad. Sci., 310*(II) (1990) 521.
3 C. Brouca-Cabarrecq and J.-C. Trombe, *C. R. Acad. Sci., 311*(II) (1990) 1179.
4 M. D. Glick, G. L. Downs and L. F. Dahl, *Inorg. Chem., 3* (12) (1964) 1712.
5 M.D. Glick and L. F. Dahl, *Inorg. Chem., 5* (2) (1966) 289.
6 Q. Chen, S. Liu and J. Zubieta, *Inorg. Chim. Acta, 175* (1990) 241.
7 D.Deguenon, *Thèse de Doctorat de l'Université,* Université Paul Sabatier, Toulouse, 1990.
8 D. Deguenon, G. Bernardinelli, J.-P. Tuchagues and P. Castan, *Inorg. Chem., 29* (1990) 3031.
9 D. Deguenon, P. Castan and F. Dahan, *Acta Crystallogr., Sect. C, 47* (1991) 433.
10 K. Yamada and Y. Hirata, *Bull. Chem. Soc. Jpn., 31* (5) (1958) 550.
11 A. Mosset, J.-J. Bonnet and J. Galy, *Acta Crystallogr., Sect. B, 33* (1977) 2633.
12 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
13 W. M. Macintyre and M. S. Werkema, *J. Chem. Phys., 42* (1964) 3563.
14 A. F. Wells, *Structural Inorganic Chemistry,* Clarendon Press, Oxford, 4th edn., 1975.
15 J.-C. Trombe, A. Gleizes and J. Galy, *Acta Crystallogr., Sect. C, 41* (1985) 1571.
16 G. Meunier and J. Galy, *Acta Crystallogr., Sect. B, 29* (1973) 1251.
17 J.-C. Trombe, J.-F. Petit and A. Gleizes, *Inorg. Chim. Acta, 167* (1990) 69.
18 *Powder Diffraction File,* Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Swarthmore, PA; Card: $K_2U_2O_7$ 29-1058.
19 M. C. Saine, *J. Less-Common Met., 154* (1989) 361.