

Supplementary Data for Thushari et al.

Microporous chiral metal coordination polymers: hydrothermal synthesis, channel engineering and thermal stability of lanthanide tartrates

Compound 1. $[\text{Ln}_2(\text{L-TAR})_3(\text{H}_2\text{O})_2]3\text{H}_2\text{O}$ Synthesis for Ln = Er Fw 868.8

$\text{Er}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$ (350mg, 1mmol) + L-tartaric acid (225mg, 1.5mmol) + KOH (110mg, 2mmol) 2mL H_2O 140°C, 2d

Yield 275mg (65% isolated yield)

TGA analysis: Fw = 868.8. - Δw 25-250°C 10.5% (5H₂O);
300-800°C 45% (organic)
Residue Er₂O₃ (44.5%)

Combustion analysis: for C₁₂H₂₂Er₂O₂₃

%C	Found 16.52	Calc. 16.59
%H	Found 2.46	Calc. 2.53

Similar preparations of phase type **1** are possible for other lanthanides with exception of Lu (pXRD is broad) i.e: La-Yb and yttrium (Y). Range of temperatures (110-180°C) and time (1d-1week) and addition of KOH or not will affect yield and crystal size for different metals.

Compound 2. $[\text{Pr}_2(\text{L-TAR})_2(\text{SUC})(\text{H}_2\text{O})_2]5.5\text{H}_2\text{O}$ Fw 829.2

$\text{Pr}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$ (320mg, 1mmol) + L-tartaric acid (150mg, 1mmol) + Succinic acid (60mg, 0.5mmol) in 5mL H_2O 110°C, 2d

Yield 220mg (55% isolated yield) pale green crystalline powder

Preparation for **2-Pr** similar to compound **1**. Erbium appears to give a related phase but is more readily contaminated by phase **1**. Use of 5mL water is advised to reduce contamination of **1** use of KOH is less necessary for the lower temperature of 110°C.

TGA analysis: Fw = 868.8. - Δw 25-310°C 17% (calc. 7.5H₂O = 16.3%)
310-800°C 43% (calc. organic = 42.7%)
Residual 40.0%, calc for Pr₂O₃ = 340/829 = 41.0%

Combustion analysis: for C₁₂H₂₇O_{23.5}Pr₂

%C	Found 17.23	Calc. 17.36
%H	Found 2.43	Calc. 3.28

The combustion analysis is rather low for H suggesting a degree of dehydration prior to analysis (sample was sent to U.K. from Hong Kong). This is consistent with the fractional occupancy of some of the disordered aqua sites of the channel.

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The thermal gravimetric analysis was conducted on a fresh sample and is compatible with up to 6 channel waters

Compound 3. [Er₂(D/L-TAR)₃(H₂O)₂]

Fw 814.8

Er(OAc)₃.xH₂O (350mg, 1mmol) + D-tartaric acid (120mg, >0.75mmol) + L-tartaric acid (120mg, >0.75mmol) + 2mL H₂O

140°C, 1d

Yield 325mg (80% isolated yield)

TGA analysis: - Δw up to 300°C negligible
 300-800°C 55% (2H₂O + organic)

Combustion analysis: for C₁₂H₂₂Er₂O₂₃

%C	Found 16.52	Calc. 16.59
%H	Found 2.46	Calc. 2.53

The TGA analysis first apparently indicated an anhydrous compound; however the crystal structure clearly revealed one bound aqua group per metal. This is actually confirmed by CHN and inclusion of the H₂O in the TGA curve above 300°C. The exceptional thermal stability of the hydrate is supported by the fact that the aqua ligand bond length in 3 is a very short 2.103Å.

Compound 4. [Er₂(m-TAR)₃.5H₂O]

Fw 868.8

The meso-tartrate analogue is synthesized in a similar manner to **3**, but with 1.5mmol meso-tartaric acid; isolated yield 330mg. The % yield can be estimated at ca. 75% since the compound is believed to be a pentahydrate based on TGA and CHN.

TGA analysis: - Δw 25- 300°C 10% (5H₂O)
 300-800°C 45% (organic)

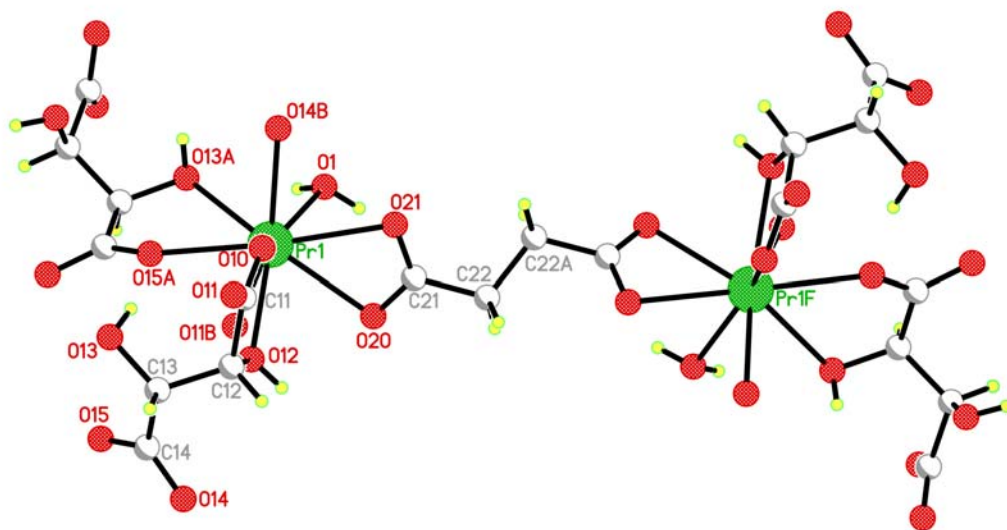
Residue 44% Er₂O₃ (382) implies original Fw 868

Combustion analysis: for C₁₂H₂₂Er₂O₂₃

%C	Found 16.19	Calc. 16.59
%H	Found 2.12	Calc. 2.53

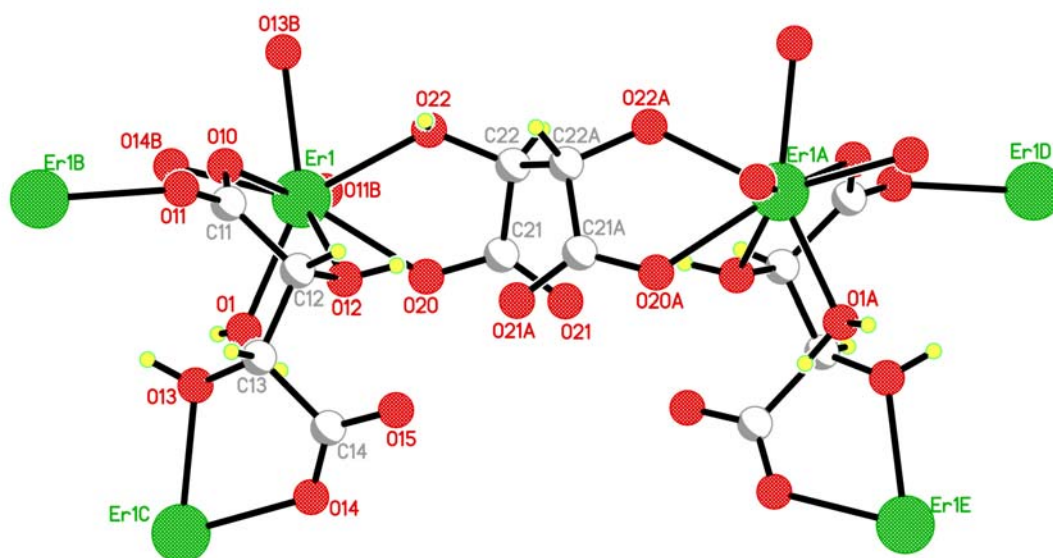
Additional Figures:

Compound 2



Details for compound 2 showing labeling scheme and μ -succinate bridge

Compound 3



Details for compound 3 showing labeling scheme and tartrate binding modes.

High Temperature Phase Transitions for 1.

VT-PXRD reveals an irreversible phase transition for 1 at ca. 100°C and a second (reversible transition at ca. 200°C. The detailed nature of these is under investigation but clearly crystallinity is retained up to 250°C and aspects of the original structure maintain integrity throughout. A single crystal structure of Gd analogue for the initial HT phase has been undertaken. The $[\text{Ln}_2(\text{L-TAR})_2]$ slab is effectively unchanged but the m2-tartrate is modified and a complex bridge (shown below) is formed. These bridges are inherently disordered by the space group symmetry which imposes a 2-fold axis through tartrate (C11-C14).

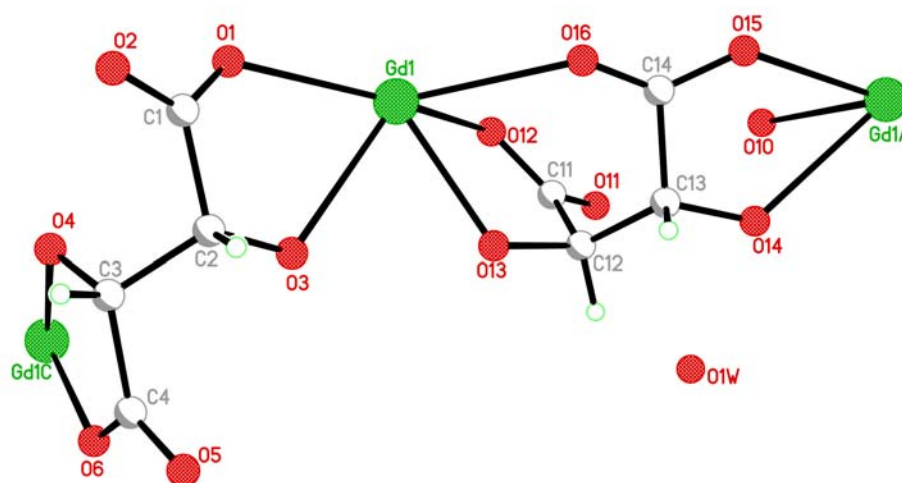
Structure of 1-HT $[\text{Ln}_2(\text{L-TAR})_3\text{H}_2\text{O}]_2\text{H}_2\text{O}$

The following compound 1-HT is irreversibly formed at 100°C; the structure is changed wrt the original μ_2 -tartrate, which becomes asymmetric and has both 1,2 and 1,3 chelation modes.

For Er the cell constants at 100K are

$$a = 5.921, b = 7.385, c = 22.036, \beta = 91.26^\circ V = 963.3 \text{ \AA}^3.$$

Space group is I2. Structure of Gd analog has been refined to ca 5% and detail shown below



200°C Phase Transition for 1:

At higher temperatures a further structural change occurs. The top 11 peaks were indexed using Cerius2 program package to the following orthorhombic cell:

$$a = 5.970, b = 11.296, c = 27.809 \text{ \AA}, V = 1875.3 \text{ \AA}^3.$$

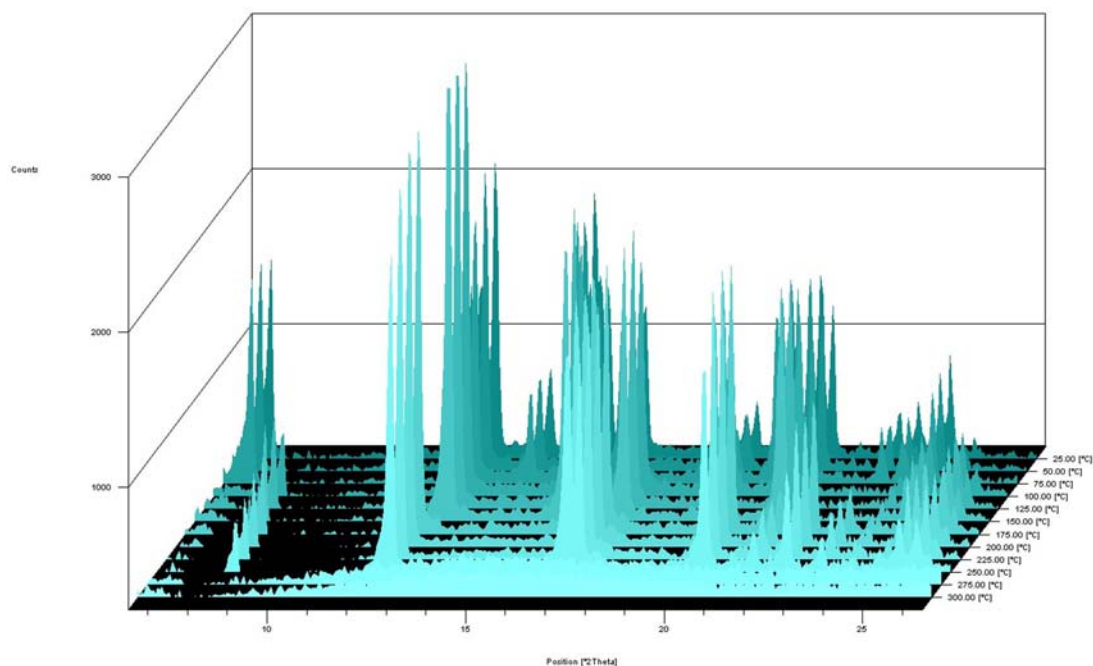
The final cell volume is thus ca. 4x the original and 2x the previous monoclinic cell.

Variable Temperature Powder X-ray Diffraction Data for 1 and 3

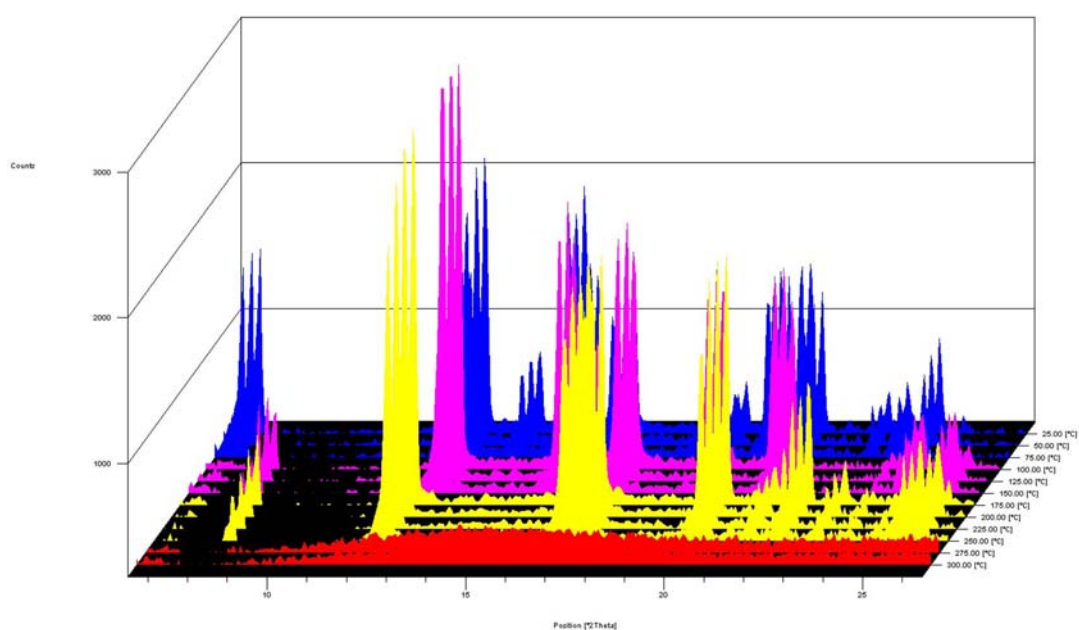
Powder patterns were measured on a PANalytical X'pert PRO diffractometer with X'Celerator real-time multi-strip (RTMS) detector and high temperature stage. Patterns were measured every 25°C, with measurement time of 1 mins and equilibration time of 5mins and heating rate of 5K min⁻¹.

Compound 1-Er:

Structural integrity of the framework is retained up to 250°C, with 2 phase transitions.

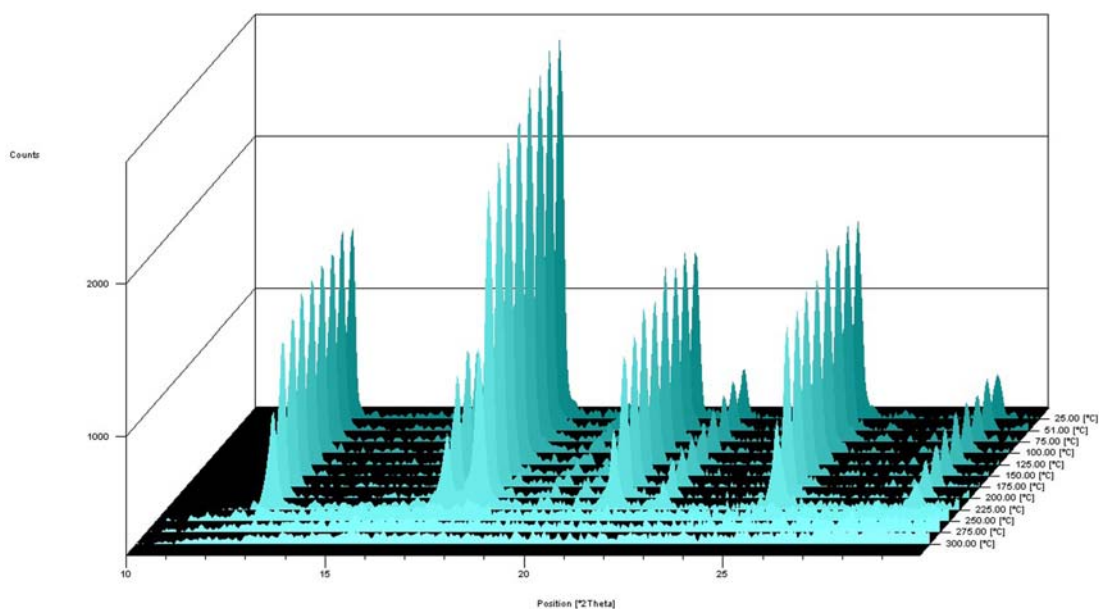


For ease of interpretation we have divided the phase transitions into different colors: Blue original (triclinic); pink (monoclinic); yellow (orthorhombic) and red (amorphous). As the cell symmetry and



Compound 3-Er:

Comment: Relatively condensed framework of the D/L-compound is quite stable, as implied by the negligible water loss to 300°C.; however its diffraction pattern is only retained up to 225°C and shows clear intensity loss above 200°C.



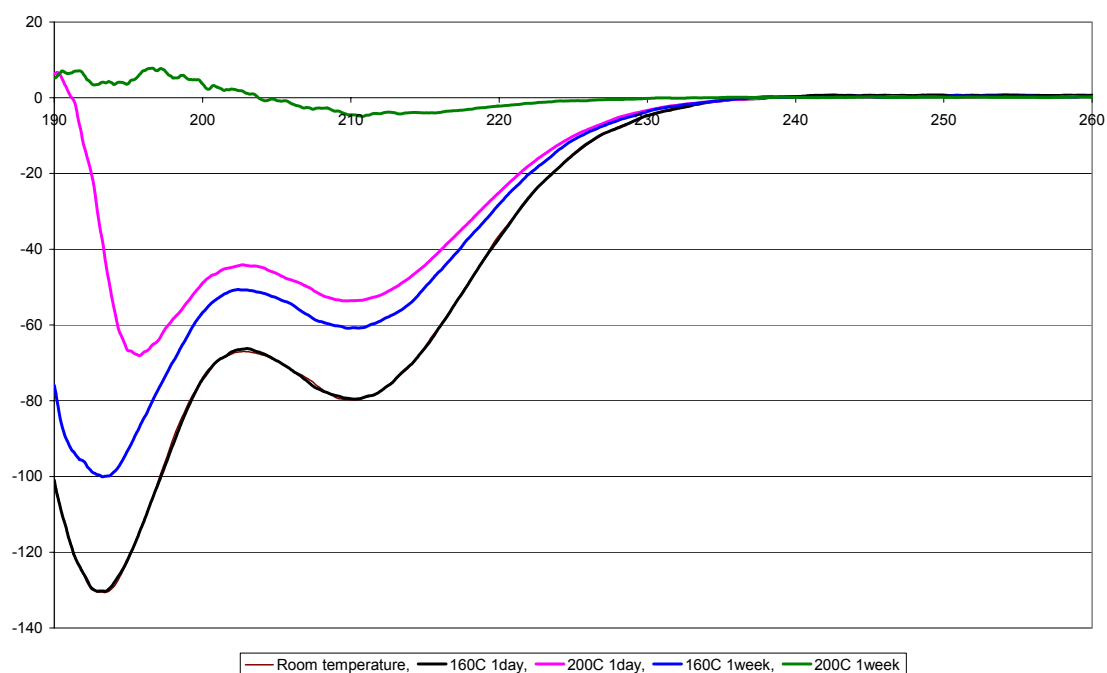
CD SPECTRA OF SODIUM L-TARTRATE SOLNS AT RT*, 160C, 200C

***The RT curve is practically superimposed on the 160C/1 day curve.**

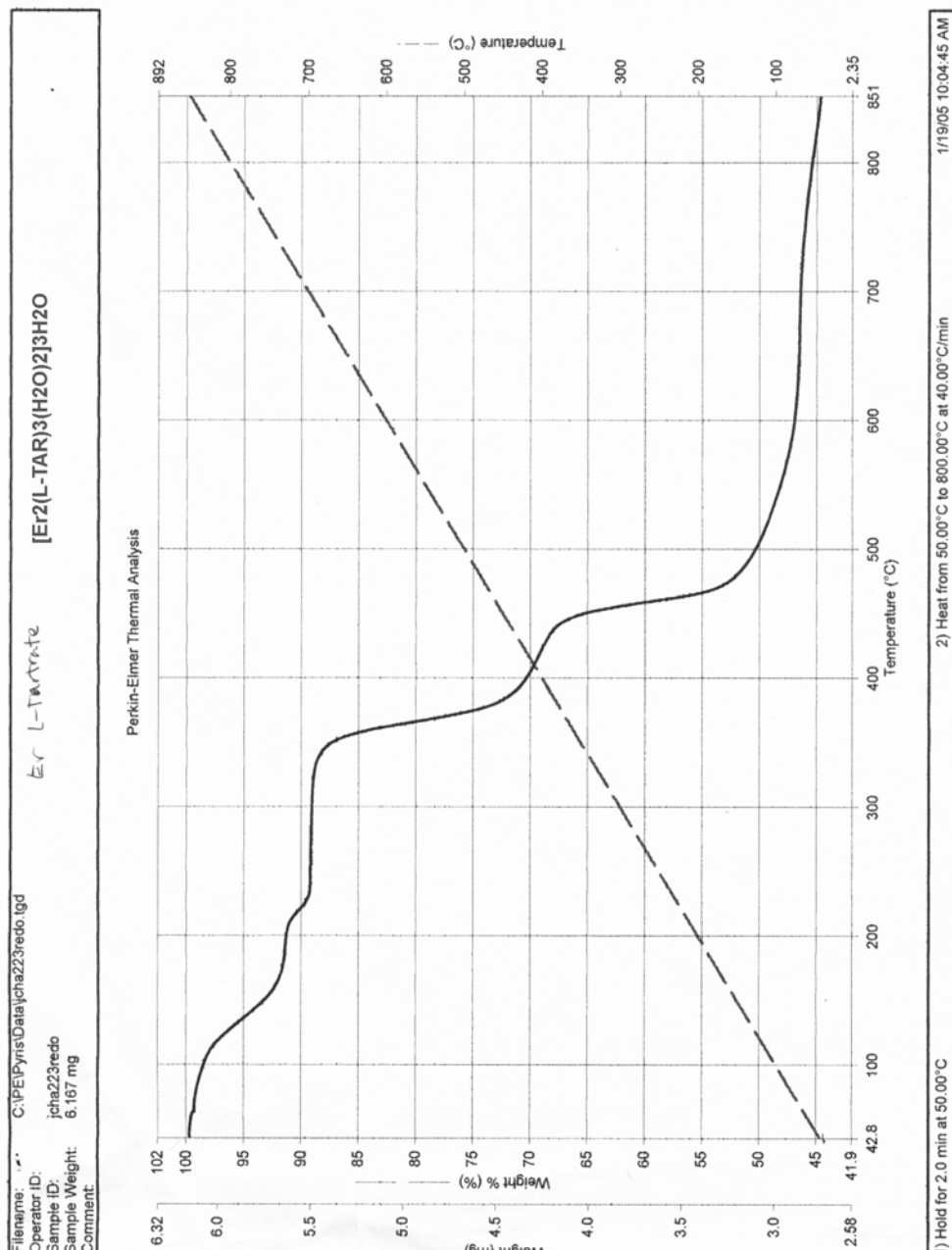
These data imply that solutions of sodium L-tartrate are relatively unchanged after periods of several days at 160°C or below. At 200°C about 50% optical activity is lost after 24h.

This puts an effective upper boundary on useful hydrothermal synthesis using L- tartrate of ca. of 160°C / 3 days or 180°C / 1 day. These conditions should be stricter if solution pH is acidic.

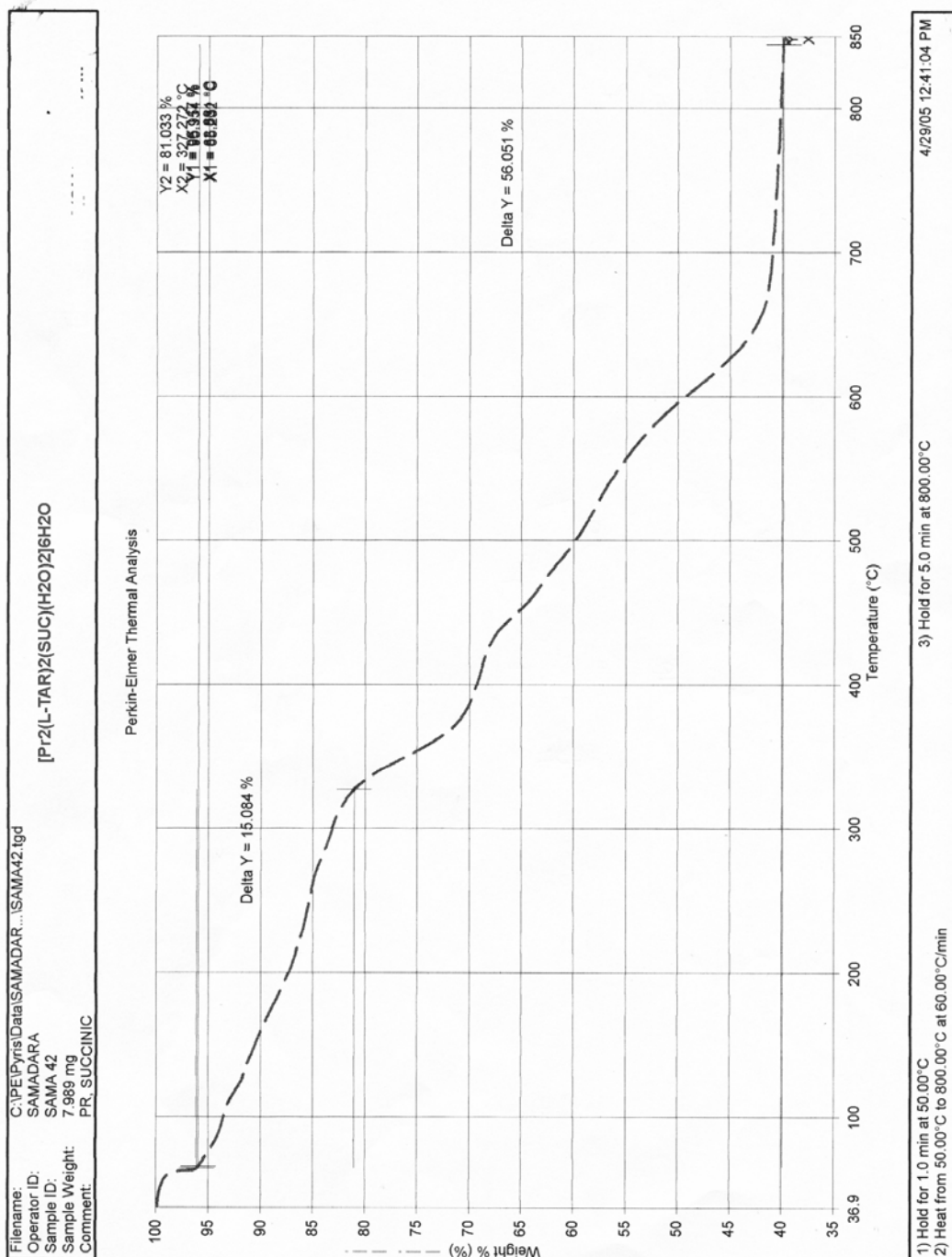
Full details about the chiral retention of L-tartrate and related chiral acids under hydrothermal conditions will be described in a subsequent publication.



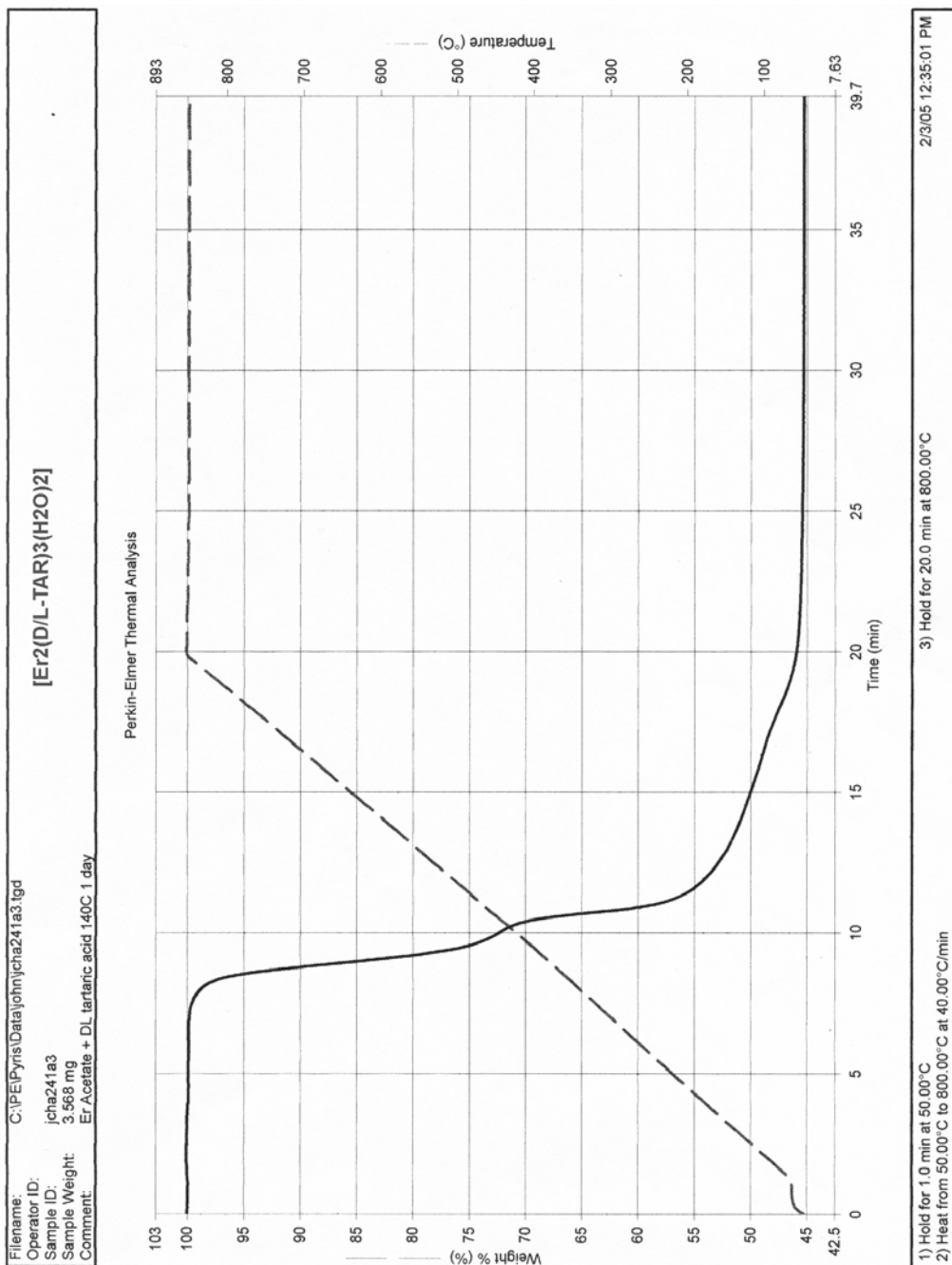
TGA Data for Compound 1



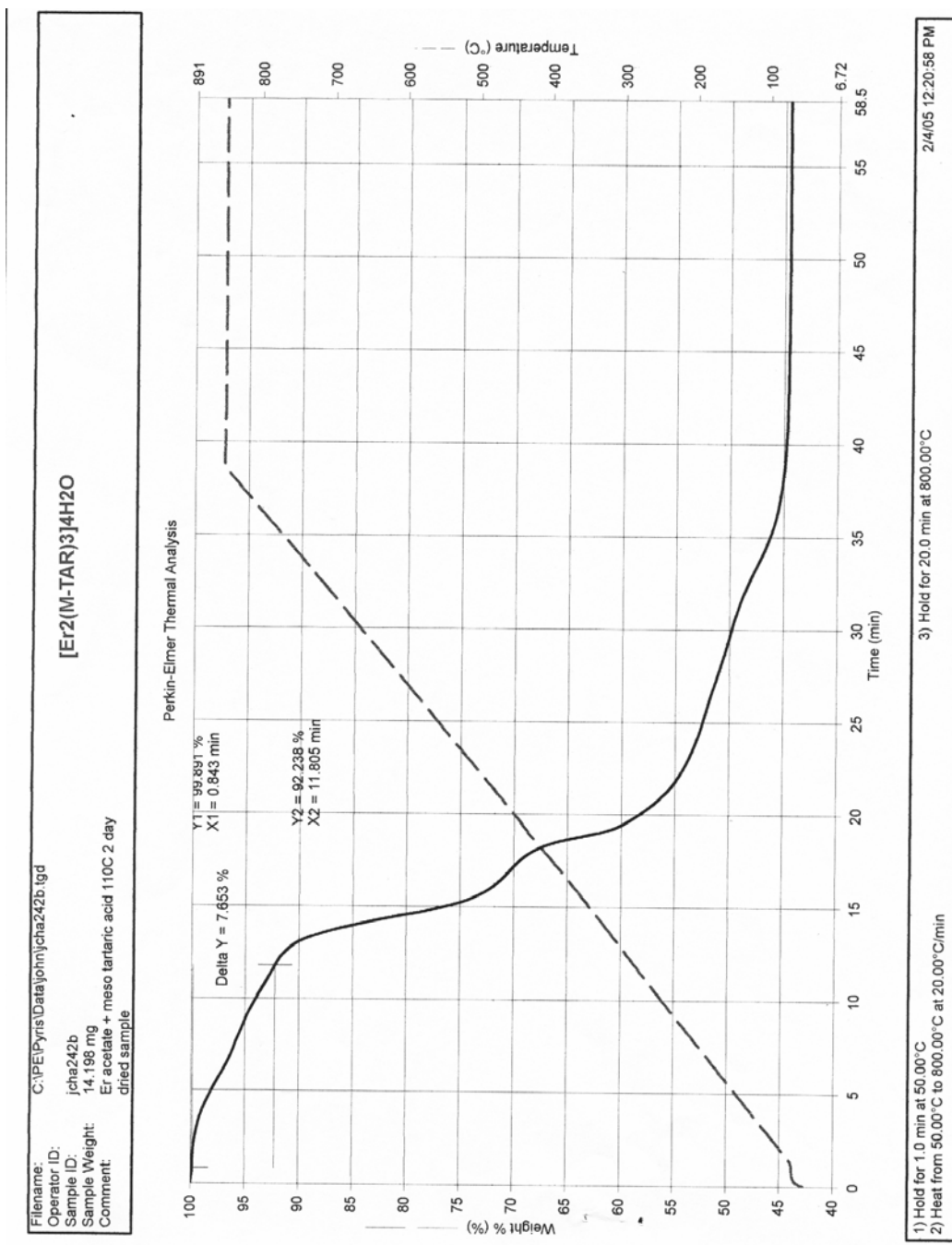
TGA Data for Compound 2



TGA Data for Compound 3



TGA Data for compound 4



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