

## Crystal Structure and Vibrational Characterization of $[\text{EMIm}]_4\text{TiCl}_6\text{Ti}_2\text{Cl}_{10}$

### Introduction

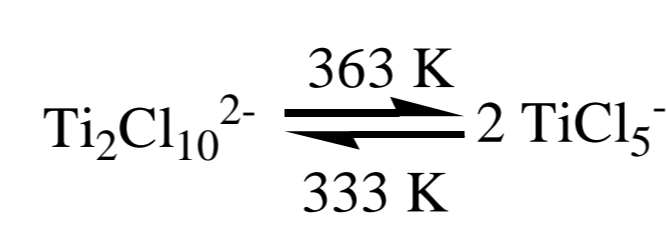
Homoleptic chlorotitanates and their adducts with acetonitrile are a class of fundamentally important coordination compounds. In general they are accessible by addition of halide ions to titanium tetrachloride. Four different homoleptic anionic complexes are known, the hexachlorotitanate  $[\text{TiCl}_6]^{2-}$ , the decachlorotitanate  $[\text{Ti}_2\text{Cl}_{10}]^{2-}$ , the pentachlorotitanate  $[\text{TiCl}_5]^-$ , the enneachlorotitanate  $[\text{Ti}_2\text{Cl}_9]^-$ , the pentachlorotitanateacetonitrile  $[\text{TiCl}_5 \cdot \text{MeCN}]^-$  and the bisacetonitriletetrachloro-titanate  $[\text{TiCl}_4 \cdot 2 \text{MeCN}]$  [1, 2]. All these complexes were prepared by using inorganic chlorides such as CsCl, quarternary ammonium or phosphonium salts and a few ionic liquids [3].

### Experimental

$[\text{EMIm}]_4[\text{TiCl}_6][\text{Ti}_2\text{Cl}_{10}]$  was prepared by addition of titanium tetrachloride to  $[\text{EMIm}]\text{Cl}$  in acetonitrile. After a reaction time of a few minutes a color change from colorless to yellow was observed. The mixture was concentrated under reduced pressure and yellow crystals of the title compound were obtained.

### Structure description

The title compound crystallizes in the monoclinic space group  $P2_1/c$  with the unit cell parameters  $a = 10.517(1) \text{ \AA}$ ,  $b = 16.275(1) \text{ \AA}$ ,  $c = 14.156(1) \text{ \AA}$ ,  $\beta = 101.16(1)^\circ$  and  $V = 2377.3(3) \text{ \AA}^3$  with  $Z = 2$ . The unit cell contains four EMIm cations and two different chlorotitanate complexes (Fig. 1). The  $[\text{Ti}_2\text{Cl}_{10}]^{2-}$  ions are located at the cell corners and in the centre of the unit cell. The  $[\text{TiCl}_6]^{2-}$  ions are situated in the middle of the cell edges whereas the ionic liquid molecules are arranged in holes of the structure (Fig. 2). The  $[\text{TiCl}_6]^{2-}$  ion has an approximately octahedral  $O_h$  symmetry with Ti—Cl bond lengths between  $2.328(1) \text{ \AA}$  and  $2.343(1) \text{ \AA}$ . The Cl—Ti—Cl angles are  $180.00(4)$  and between  $88.40(4)$  and  $91.60(4)$ . The edge-sharing dioctahedral  $[\text{Ti}_2\text{Cl}_{10}]^{2-}$  units show Ti—Cl bond lengths between  $2.227(1)$  and  $2.536(1) \text{ \AA}$ . Titanium has a distorted octahedral coordination sphere due to the dichloro-bridged connection. Particularly the bond angle involving the bridging chlorine is rather deformed with a Cl—Ti—Cl angle of  $168.29(5)$ . Furthermore, the dimer-monomer conversion (Equation 1) from the decachlorodititanate to the pentachlorotitanate has been investigated by differential scanning calorimetry (DSC) and temperature dependent Raman scattering (Figure 3, Figure 4).



Equation. 1

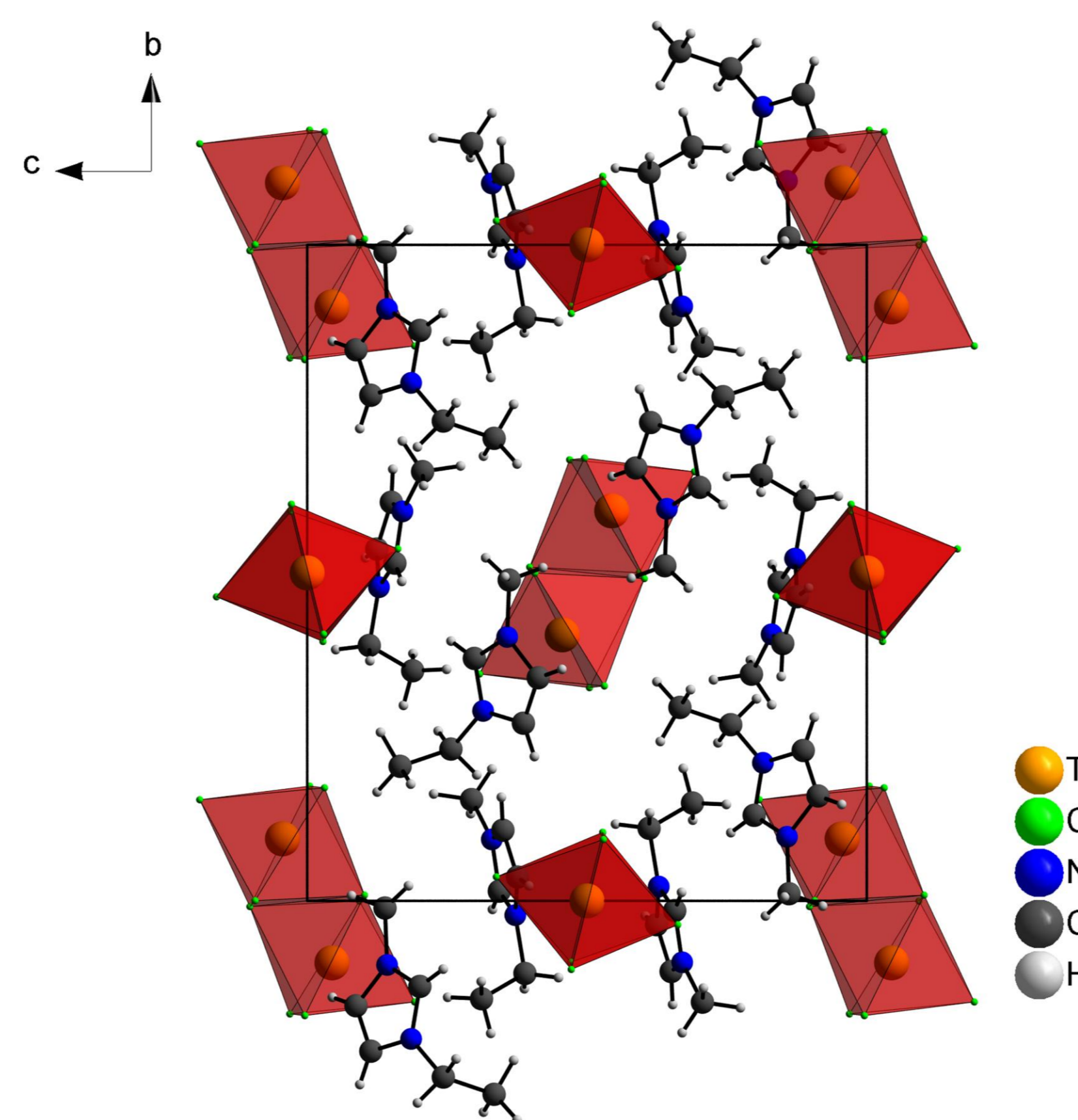


Fig. 1 Perspective view of the unit cell along a-axis

Tab. 1 Crystallographic data for  $[\text{EMIm}]_4[\text{TiCl}_6][\text{Ti}_2\text{Cl}_{10}]$

Empirical formula	$\text{C}_{24}\text{H}_{44}\text{N}_8\text{Ti}_3\text{Cl}_{16}$
Formula weight / $\text{g mol}^{-1}$	1155.57
Crystal system	monoclinic
Space group	$P2_1/c$
$a / \text{ \AA}$	10.517(1)
$b / \text{ \AA}$	16.275(1)
$c / \text{ \AA}$	14.156(1)
$\beta / ^\circ$	101.16(1)
Volume / $\text{ \AA}^3$	2377.3(3)
$Z$	2
$D_{\text{calc}} / \text{ g cm}^{-3}$	1.614
$F(000)$	1164
$\Theta_{\text{min, max}} / ^\circ$	1.93, 25.03
Index ranges	$-12 \leq h \leq 11$ $-19 \leq k \leq 19$ $-16 \leq l \leq 16$
Unique reflections	4198
Data / restraints / parameters	4198 / 0 / 320
Goodness-of-fit on $F^2$	1.056
R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0438$ $wR2 = 0.0978$
R indices (all data)	$R1 = 0.0511$ $wR2 = 0.1016$
Larg diff. peak and hole / $e \text{ \AA}^{-3}$	1.390 and $-1.009$

Tab. 2 Selected bond length [ $\text{ \AA}$ ] and angles [ $^\circ$ ] for  $[\text{EMIm}]_4[\text{TiCl}_6][\text{Ti}_2\text{Cl}_{10}]$

Ti—Cl1	2.3289(10)	Ti—Cl1 <sup>i</sup>	2.3290(10)
Ti—Cl2	2.3425(9)	Ti—Cl2 <sup>i</sup>	2.3425(9)
Ti—Cl3	2.3277(10)	Ti—Cl3 <sup>i</sup>	2.3276(10)
Ti2—Cl8	2.2274(12)	Ti2—Cl5	2.2705(12)
Ti2—Cl4	2.2914(12)	Ti2—Cl6	2.2983(12)
Ti2—Cl7	2.4867(10)	Ti2—Cl7 <sup>ii</sup>	2.5355(10)
Cl7—Ti2 <sup>ii</sup>	2.5356(10)		
Cl3—Ti—Cl3	180.00(4)	Cl3—Ti—Cl1	89.87(5)
Cl3—Ti—Cl1	90.13(5)	Cl3—Ti—Cl1 <sup>i</sup>	90.13(5)
Cl3—Ti—Cl1 <sup>i</sup>	89.87(5)	Cl1—Ti—Cl1 <sup>i</sup>	180.00(8)
Cl3—Ti—Cl2 <sup>i</sup>	89.18(4)	Cl3—Ti—Cl2 <sup>i</sup>	90.82(4)
Cl1—Ti—Cl2 <sup>i</sup>	91.60(4)	Cl1 <sup>i</sup> —Ti—Cl2 <sup>i</sup>	88.40(4)
Cl3 <sup>i</sup> —Ti—Cl2	90.82(4)	Cl3—Ti—Cl2	89.18(4)
Cl1—Ti—Cl2	88.40(4)	Cl1 <sup>i</sup> —Ti—Cl2	91.60(4)
Cl2 <sup>i</sup> —Ti—Cl2	180.0	Cl8—Ti2—Cl2	100.62(5)
Cl8—Ti2—Cl4	93.47(5)	Cl5—Ti2—Cl4	91.18(5)
Cl8—Ti2—Cl6	93.26(5)	Cl5—Ti2—Cl6	91.04(5)
Cl4—Ti2—Cl6	172.40(5)	Cl8—Ti2—Cl7	91.07(4)
Cl5—Ti2—Cl7	168.29(5)	Cl4—Ti2—Cl7	87.19(4)
Cl6—Ti2—Cl7	89.17(4)	Cl8—Ti2—Cl7 <sup>ii</sup>	169.82(5)
Cl5—Ti2—Cl7 <sup>ii</sup>	89.55(4)	Cl4—Ti2—Cl7 <sup>ii</sup>	85.57(4)
Cl6—Ti2—Cl7 <sup>ii</sup>	87.17(4)	Cl7—Ti2—Cl7 <sup>ii</sup>	78.76(3)
Ti2—Cl7—Ti2 <sup>ii</sup>	101.24(3)		

Symmetry code: i)  $-x, -y, 1-z$ ; ii)  $-1-x, -y, -z$

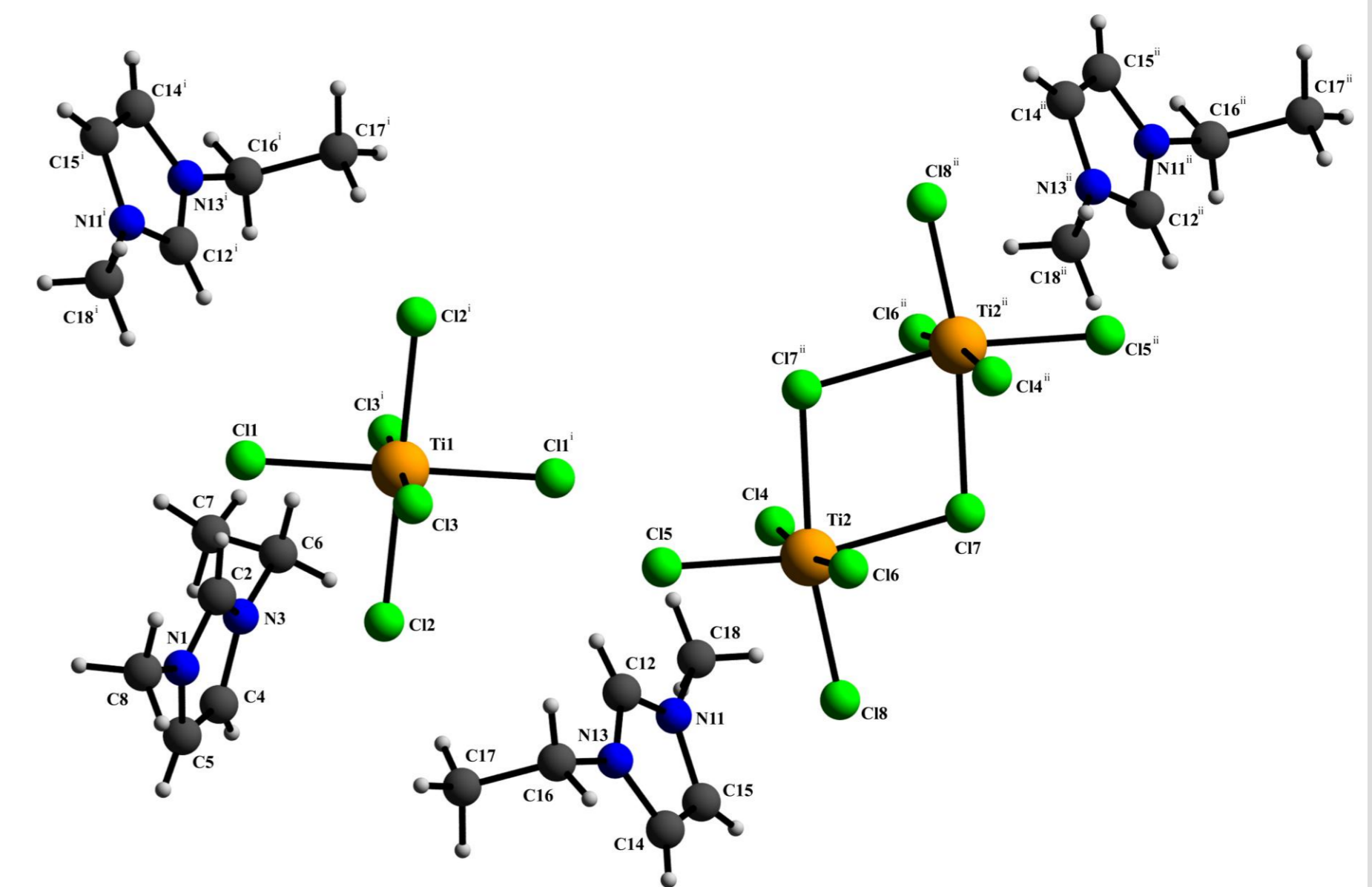


Fig. 2 Coordination Polyeder in  $[\text{EMIm}]_4[\text{TiCl}_6][\text{Ti}_2\text{Cl}_{10}]$

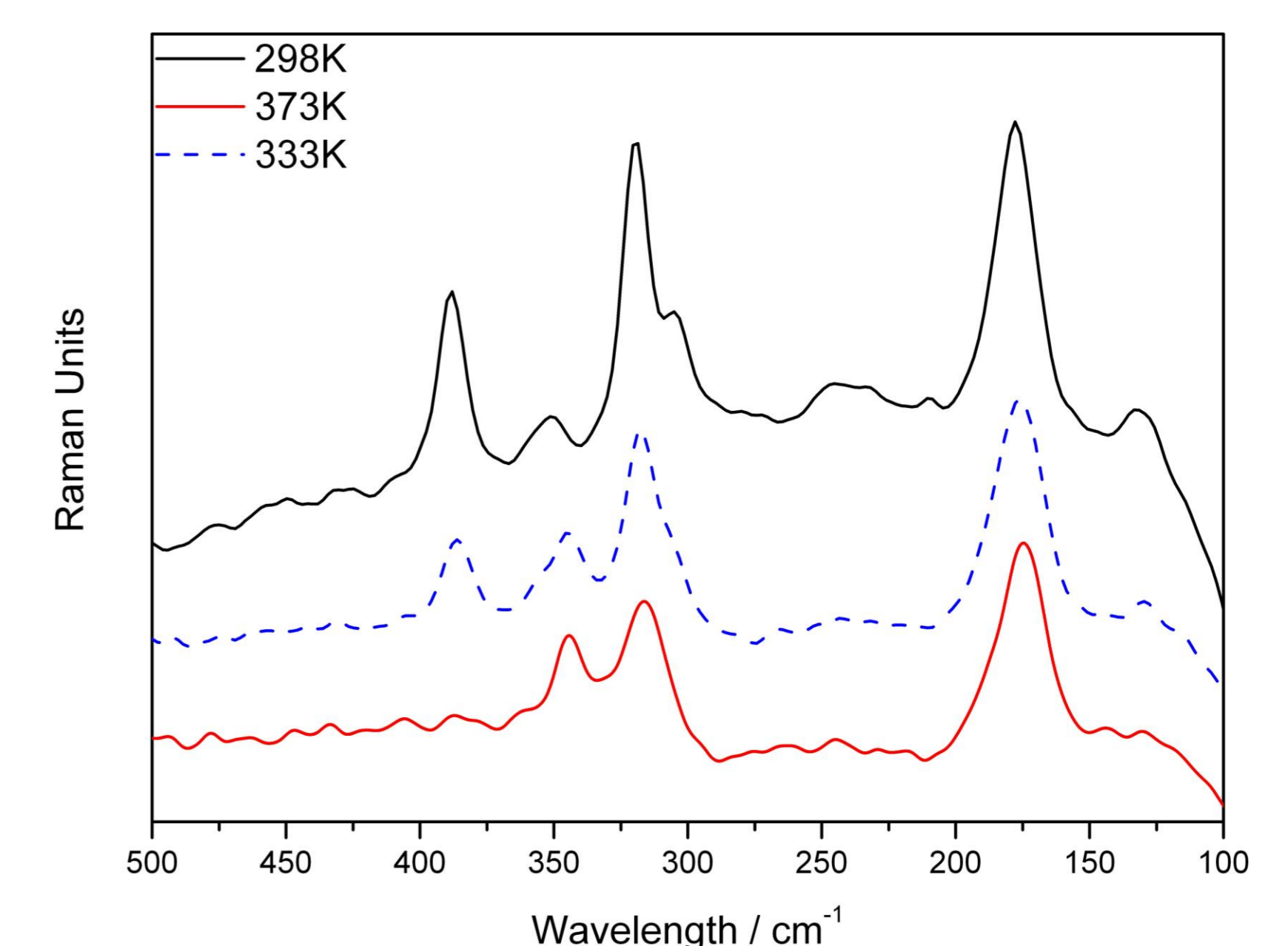


Fig. 3 FT-Raman spectra compound III at different temperatures

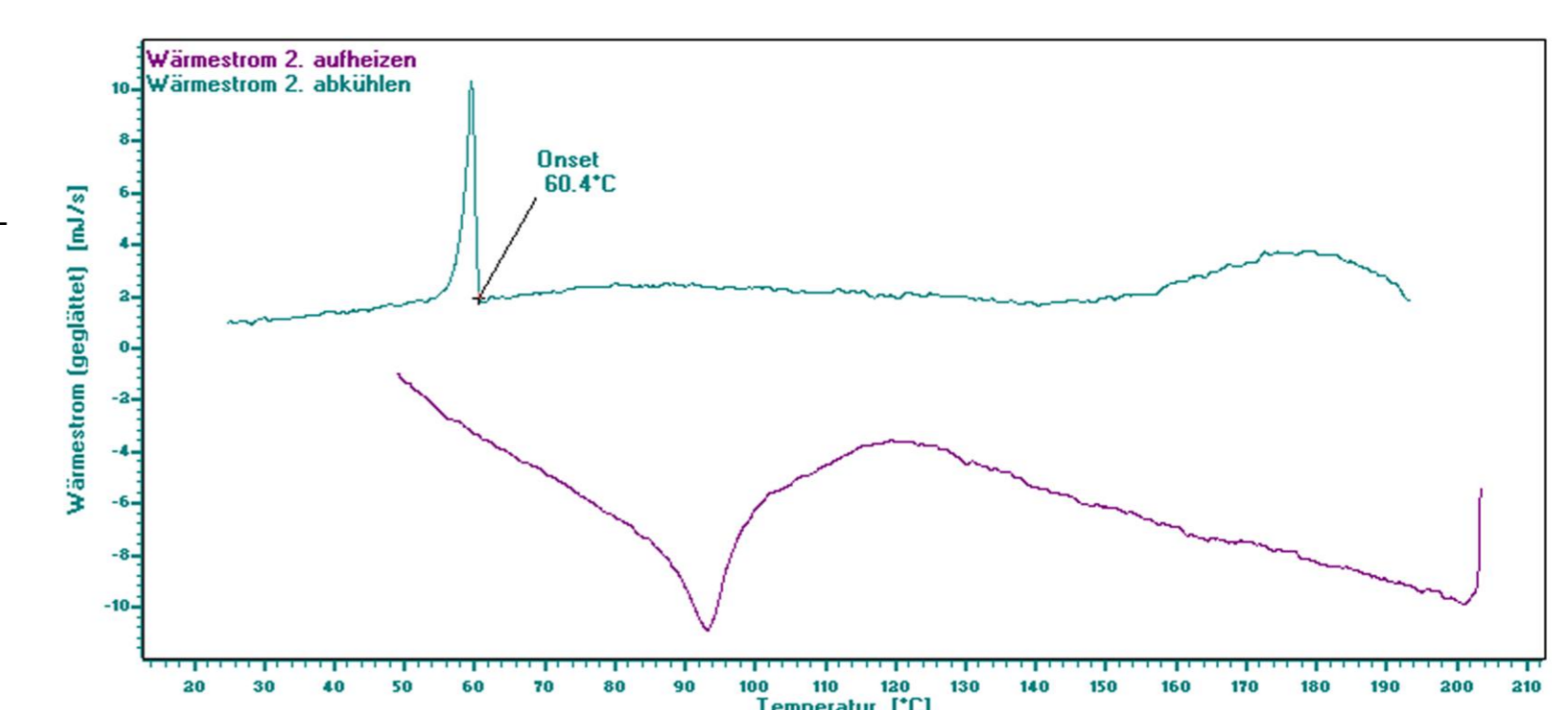


Fig. 4 Differential scanning calorimetry results

Tab. 2 Raman frequencies ( $\text{cm}^{-1}$ )

$[\text{EMIm}]_4\text{TiCl}_6\text{Ti}_2\text{Cl}_{10}$	$\text{TiCl}_6$	$\text{TiCl}_6$	$\text{Ti}_2\text{Cl}_{10}$
298 K	373 K	[4]	[5]
387			389
350	350		355
320	320	320	317
305			308
242	242		252
176	176	173	180

### References

- [1] T. J. Kistenmacher, G. D. Stucky, *Inorg. Chem.* **1971**, *10*, 122-132
- [2] A. Feltz, *Z. Anorg. Allg. Chem.* **1965**, *338*, 147-154
- [3] G. Laus, G. Bentivoglio, K. Wurst, H. Schottenberger, G. Nauer, *Z. Kristallogr.* **2005**, *NCS 220*, 577-578
- [4] R. J. H. Clark, L. Maresca, R. J. Puddephatt, *Inorg. Chem.* **1968**, *7*, 1603
- [5] F. Demiray, W. Brockner, *Spectrochim. Acta* **1978**, *35A*, 659-662
- [6] C. S. Creaser, J. A. Creighton, *J. C. S. Dalton* **1975**, 1402-1405