

# $^{241}\text{Am}$ doped Tb complexes of 5,5'-azobis[1H-tetrazol-1-ide] as example for overcoming the Gd-break in lanthanide coordination chemistry

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## Motivation:

The aim of this study was to investigate how the coordination chemistry of known lanthanide complexes is influenced by an external stimulus, for example by admixture of a 5f element.

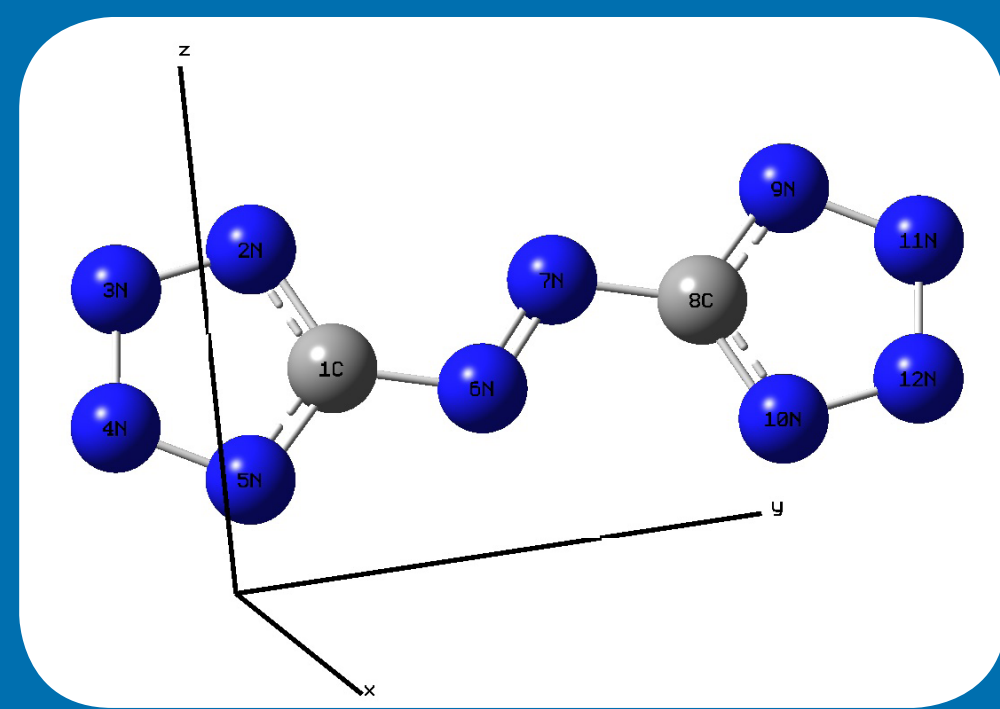


Fig. 1: DFT calculation of  $\text{ZT}^{2-}$ .

## Synthesis of the ligand $\text{Na}_2\text{ZT} \cdot 2\text{H}_2\text{O}$ :

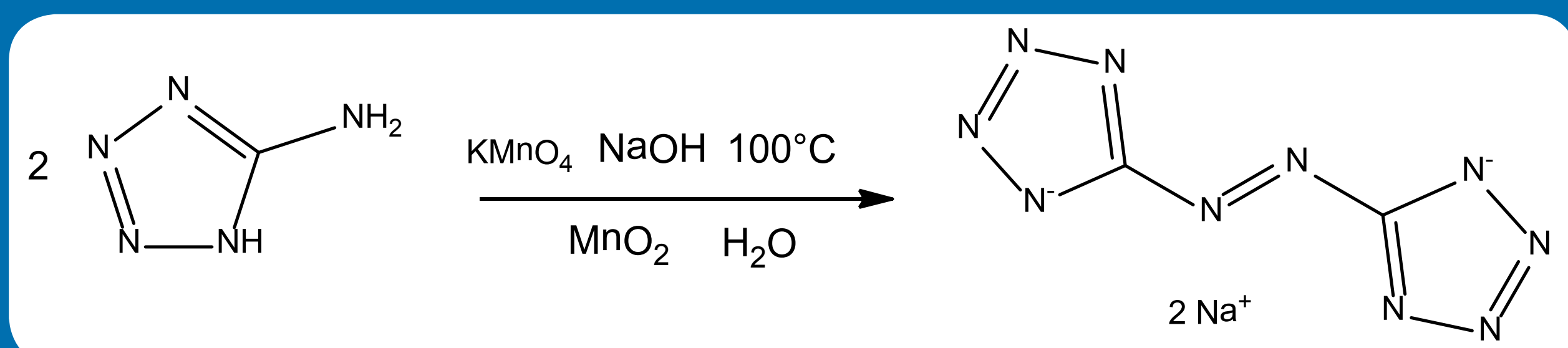


Fig. 2: Synthesis of  $\text{Na}_2\text{ZT} \cdot 2\text{H}_2\text{O}$  according to Thiele and Singh et al.

Disodium 5,5'-azobis[1H-tetrazol-1-ide] dihydrate ( $\text{Na}_2\text{ZT} \cdot 2\text{H}_2\text{O}$ ) was prepared according to Thiele [1] and Singh et al. [2] by oxidation of 1H-tetrazol-5-amine monohydrate with  $\text{KMnO}_4$  in aqueous solution of  $\text{NaOH}$ , and subsequent partial dehydration of the pentahydrate, as described in [3].

## Synthesis of $\text{Tb}_2\text{ZT}_3$ complexes:

200 mg  $\text{Na}_2\text{ZT} \cdot 2\text{H}_2\text{O}$  (0,81 mmol) were dissolved in 4 mL water, 120,75 mg  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0,266 mmol) were dissolved in 1 mL water. These two solutions were mixed and after 10 minutes the residue was filtrated over a syringe filter. The clear brownish solution was allowed to stand overnight and single crystals were obtained.

## Synthesis of $^{241}\text{Am}$ spiked $\text{Tb}_2\text{ZT}_3$ complexes:

In addition to the above described procedure the mixture was spiked with 20  $\mu\text{L}$  of a stock solution of neutron activated  $\text{Tb}(\text{NO}_3)_3$  ( $^{160}\text{Tb}$ ) dissolved in water and 20  $\mu\text{L}$  of  $^{241}\text{Am}$  in diluted nitric acid [pH~2].

## Gamma spectrometry:

Activities of  $^{160}\text{Tb}$  and  $^{241}\text{Am}$  were determined for both the initial mixture of solutions and the crystals (after washing the surface) by gamma spectrometry. The samples were filled to 5 mL with diluted hydrochloric acid, which dissolves them completely, and measured in fixed geometries.

Activities were decay corrected for the second measurement.

## Methods of characterization:

The ligands were characterized using,  $^{13}\text{C}$ -NMR, ATR mid-range FTIR, ATR far-range FTIR and Raman spectroscopy, the complexes using single crystal X-ray diffraction, ATR mid-range FTIR, ATR far-range FTIR and Raman spectroscopy. Gamma spectrometry of the activated samples was performed on a 226  $\text{cm}^3$  HPGc detector (Canberra™, detector model GC5020; 2.0 keV resolution at the 1332 keV  $^{60}\text{Co}$  peak; 52.8% relative efficiency), connected to a PC-based multi-channel analyser with preloaded filter. For qualitative interpretation of the IR and Raman spectra of the ligand also DFT optimisation followed by frequency analysis with Gaussian 09 was performed [4]. Level of theory: DFT B3LYP, Basis set: 6-311++g(d,p).

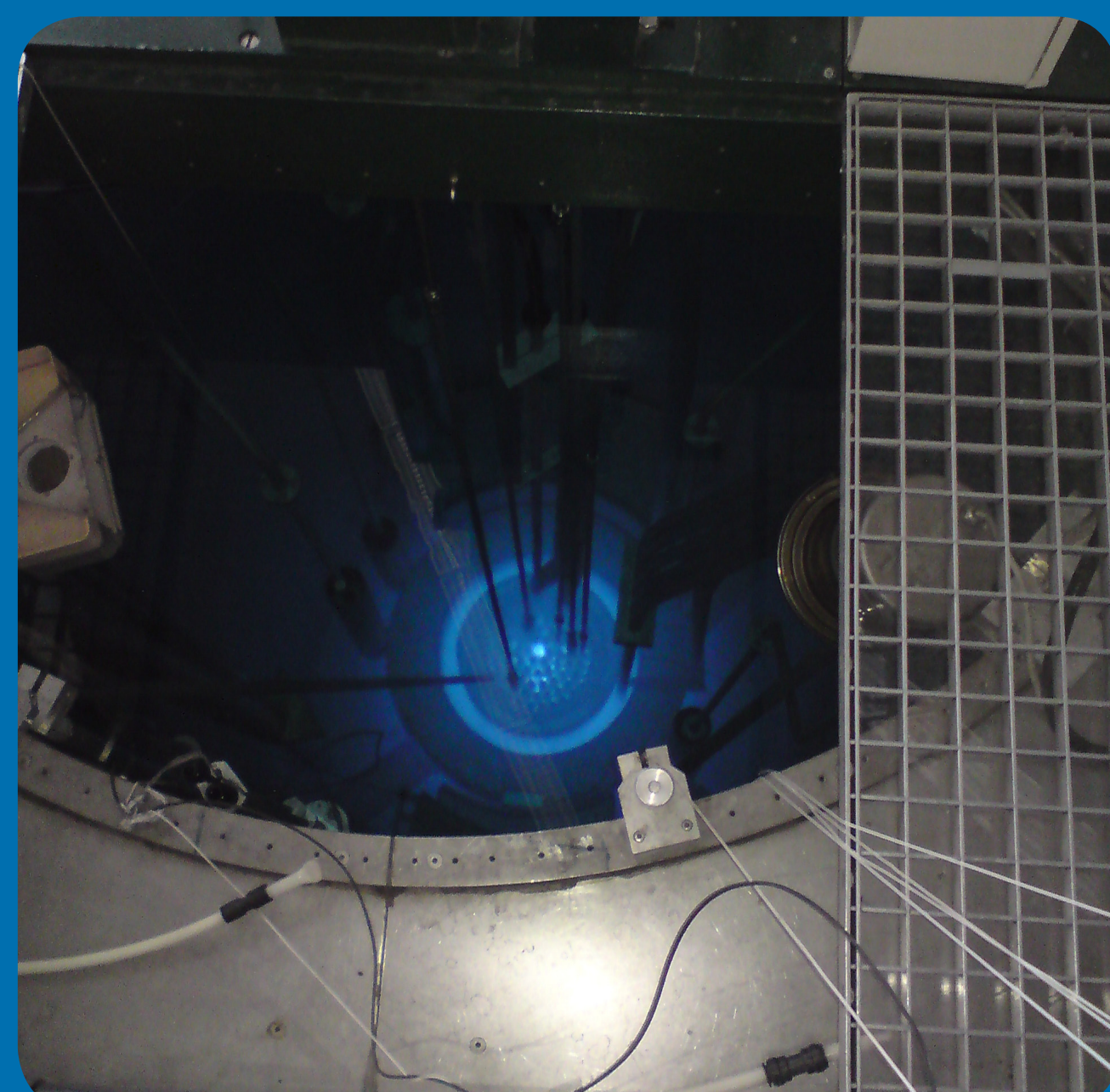


Fig. 3: Cherenkov radiation of TRIGA Mark II reactor at the Institute of Atomic and Subatomic Physics at Vienna University of Technology at 250kW.



Fig. 4: Inserting irradiation sample holder into the first of the five reflector irradiation tubes of the TRIGA Mark II reactor, filled with a  $\text{Tb}(\text{NO}_3)_3$  sample.

## Results:

### Gamma spectrometry:

Solution shortly after mixture:  
 $^{241}\text{Am}$ : 0.1090 cts/s /  $^{160}\text{Tb}$ : 0.4668 cts/s  
dissolved crystal after XRD-measurement:  
 $^{241}\text{Am}$ : 0.1358 cts/s /  $^{160}\text{Tb}$ : 0.2060 cts/s

We have an activity ratio of 4.28 for the solution and 1.52 for the crystal. The comparison of these results leads to the presumption that the Tb crystal obviously incorporates  $^{241}\text{Am}$  preferred. The measurement uncertainty is about 3% relative.

## NMR - results:

Disodium 5,5'-azobis[1H-tetrazol-1-ide] dihydrate:  
 $^{13}\text{C}$ -NMR (50 MHz,  $\text{DMSO}-d_6$ , 298K):  $\delta = 173.33$  ppm

## IR - results:

Disodium 5,5'-azobis[1H-tetrazol-1-ide] dihydrate:  
 $\nu$ : 1430, 1401, 1196, 1163, 1051, 883, 773, 739, 732  $\text{cm}^{-1}$

## Raman - results:

Disodium 5,5'-azobis[1H-tetrazol-1-ide] dihydrate:  
 $\nu$ : 920, 1049, 1072, 1376, 1415, 1478  $\text{cm}^{-1}$

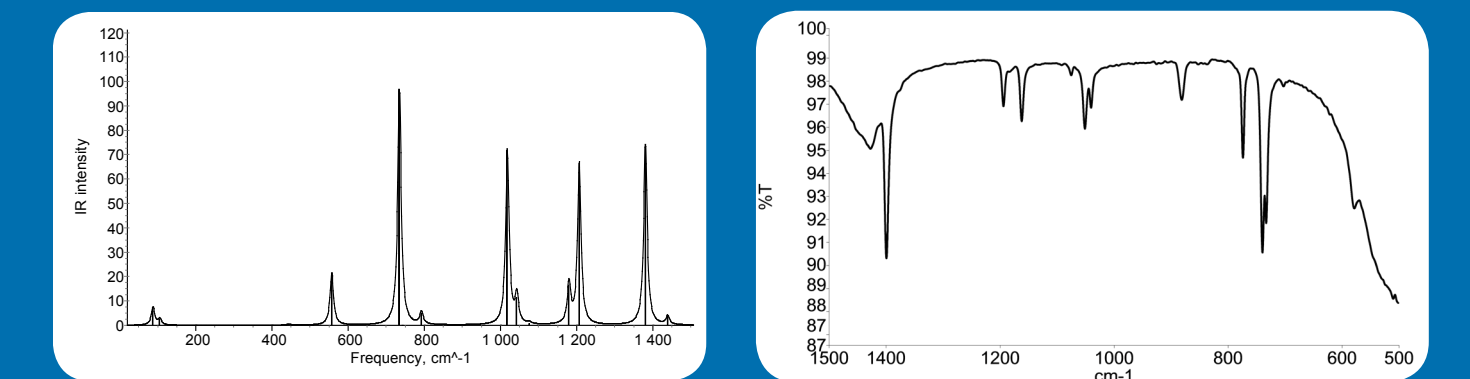


Fig. 5/6: Calculated (left) vs. measured (right) IR spectra of  $\text{ZT}^{2-}$  respectively  $\text{Na}_2\text{ZT} \cdot 2\text{H}_2\text{O}$ .

## X-ray single crystal diffraction results:

	$^{241}\text{Am}_x\text{Tb}_{1-x}(\text{H}_2\text{O})_7\text{ZT} \cdot x\text{H}_2\text{O}$
Space group	$P\bar{1}$
cell lengths [Å]	$a = 8.9817(2)$ $b = 9.7096(2)$ $c = 22.7609(5)$
cell angles [°]	$\alpha = 96.8049(10)$ $\beta = 96.700(2)$ $\gamma = 95.3669(10)$
cell volume [Å <sup>3</sup> ]	$V = 1643.92$



Fig. 7: Crystal of  $^{241}\text{Am}$  spiked  $^{241}\text{Am}_x\text{Tb}_{1-x}(\text{H}_2\text{O})_7\text{ZT}$ .

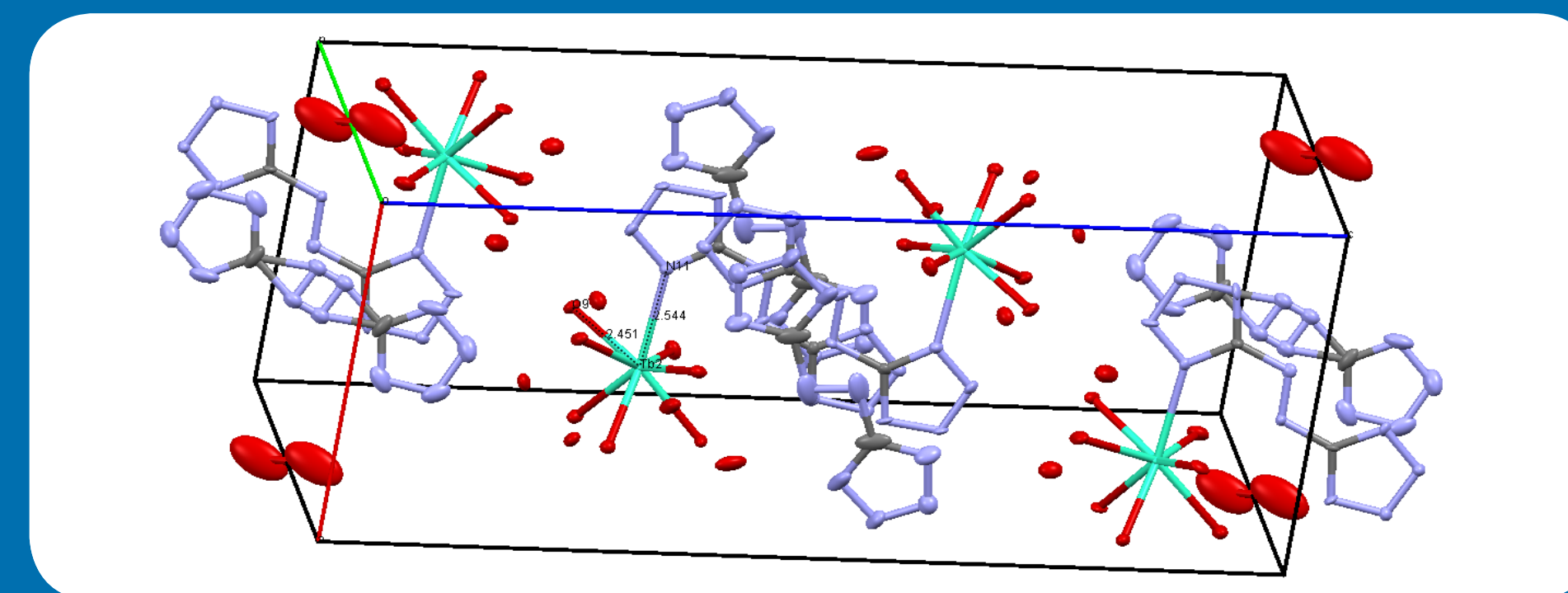


Fig. 8: Crystal structure of  $^{241}\text{Am}$  spiked  $^{241}\text{Am}_x\text{Tb}_{1-x}(\text{H}_2\text{O})_7\text{ZT}$ , displayed in Fig. 7.

## Conclusion:

Based on the experimental data, we propose that the observed crystal consists of an  $^{241}\text{Am}$  enriched  $^{241}\text{Am}_x\text{Tb}_{1-x}(\text{H}_2\text{O})_7\text{ZT}$  complex. The increased gamma counts of  $^{241}\text{Am}$  detected in the crystal supports our hypothesis. As the crystal structure reveals a coordinative bond is formed between the ZT ligand and the lanthanide / actinide center. This is in contrast to the expected result according to the Gd-break described in literature. [3; 5]

## Acknowledgement:

Thanks for financial support to the Austrian Science Fund (FWF) project P24955-N28. Thanks are also due to the X-ray center of Vienna University of Technology (Dr. Klaudia Hradil). The computational results presented have been achieved using the Vienna Scientific Cluster.

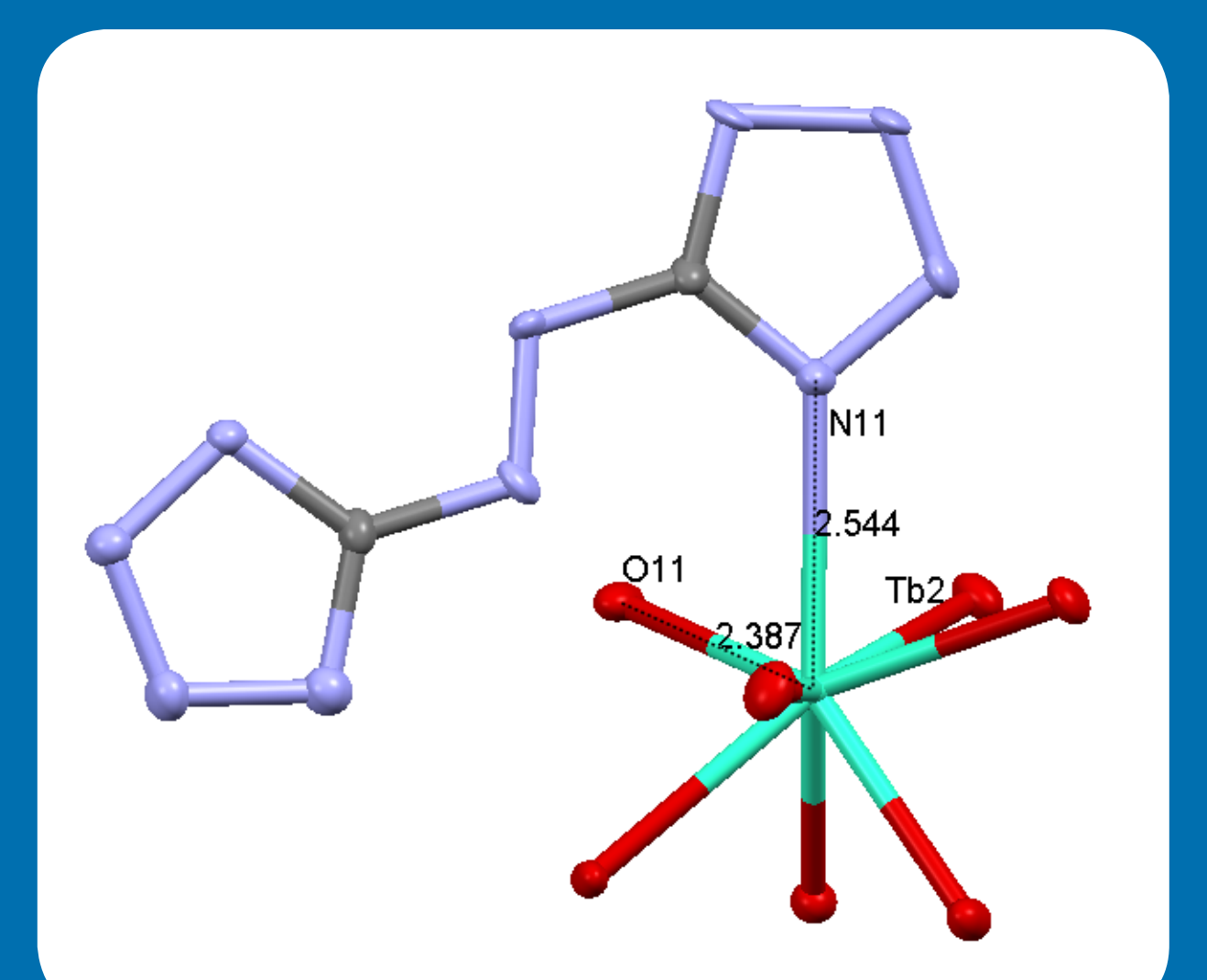


Fig. 9: Detail of crystal structure of  $^{241}\text{Am}$  spiked  $\text{Tb}(\text{H}_2\text{O})_7\text{ZT}$  with displayed bond-lengths.