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J. Chem. Research (M), 1999, 1938–1951

One-dimensional Coordination Polymer $\{[Tm_2(ttha)(H_2O)_6Tm_2(ttha)(H_2O)_4]\cdot 21H_2O\}_n$: Synthesis, Crystal Structure, Thermal Behavior and Magnetism (H_6ttha = Triethylenetetraminehexaacetic Acid)

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The reaction of H_6ttha and Tm_2O_3 gives a chain compound determined by X-ray diffraction; its thermal behavior and magnetic properties are also studied.

Polyaminepolycarboxylic acids and their derivatives are very important chelating agents for metal ions, and the diethylenetriaminepentaacetic acid (H_5dtpa) complex with gadolinium has been used as MRI agent in the NMR diagnosing of tumors.[3,4] Having the similar coordination ability as H_5dtpa toward lanthanide ions, triethylenetetraminehexaacetic acid (H_6ttha) can also strongly chelate with lanthanide ions, and its complex with gadolinium may also be used as an image-enhancing agent. Only very recently, crystallographic data on such complexes has been reported.[7–14] All these complexes have a 1 : 1 molar ratio between lanthanide ion and ttha, and their structures are either monomeric[7–12] or dimeric.[13,14] Here, we report a novel one-dimensional chain coordination polymer $\{Tm_2(ttha)(H_2O)_6Tm_2(ttha)(H_2O)_4]\cdot 21H_2O\}_n$ with a 2 : 1 molar ratio between lanthanide ion and ttha (Fig. 2).

The process of thermal decomposition of the title compound can be described as follows:

$$Tm_2(ttha)(H_2O)_6Tm_2(ttha)(H_2O)_4\cdot 21H_2O \xrightarrow[42.1-96.3\ ^\circ C]{-11H_2O} Tm_2(ttha)Tm_2(ttha)(H_2O)_{20} \xrightarrow[113.3-141.8\ ^\circ C]{-20H_2O} Tm_2(ttha)Tm_2(ttha) \xrightarrow[380.4-450.7\ ^\circ C]{} Tm_2O_3Tm_2(ttha) \xrightarrow[>517\ ^\circ C]{} 2Tm_2O_3$$

Variable-temperature magnetic susceptibility data indicates the presence of an overall antiferromagnetic behaviour with intra and/or inter-molecular contributions. This may be caused by the splitting of the ligand field around Tm^{3+}. There is also likely to be antiferromagnetic coupling between Tm^{3+} ions.[21]

Crystal Data for $C_{36}H_{110}N_8O_{55}Tm_4$: $M_r = 2211$, triclinic, space group $P\bar{1}$, $a = 10.9977(4)$, $b = 12.7668(8)$, $c = 14.6537(12)$ Å, $\alpha = 75.717(6)$, $\beta = 85.371(5)$, $\gamma = 71.605(4)^\circ$, $V = 1892.0(2)$ Å^3, $Z = 1$, $D_c = 1.941$ Mg m^{-3}, $\mu = 4.78$ mm^{-1}, F(000) = 1098. Full-matrix least-squares refinement gave final $R1 = 0.0294$, $wR2 = 0.0632$ for 8656 observed reflections [$I > 2\sigma(I)$].

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Techniques used: FTIR, thermogravimetry, magnetic susceptibility, single crystal diffraction

Tables 1–3: Details of crystal data and refinement, selected bond lengths and angles and hydrogen bonding interactions.

Fig. 1: An ORTEP drawing of the complex $\{[Tm_2(ttha)(H_2O)_6$-$Tm_2(ttha)(H_2O)_4)\cdot 21H_2O\}_n$ with 30% probability ellipsoids

Fig. 3: Coordination polyhedron of Tm1 and Tm2

Fig. 4: Packing diagram of the $\{[Tm_2(ttha)(H_2O)_6Tm_2(ttha)(H_2O)_4]\cdot 21H_2O\}_n$ chain viewed down the *b* direction

Fig. 5: Thermogravimetric analysis data for $\{[Tm_2(ttha)(H_2O)_6$-$Tm_2(ttha)(H_2O)_4)\cdot 21H_2O\}_n$

Fig. 6: Plot of $\chi_m T$ *versus* T (△) and $1/\chi_m$ *versus* T (○) for the Tm_2 unit

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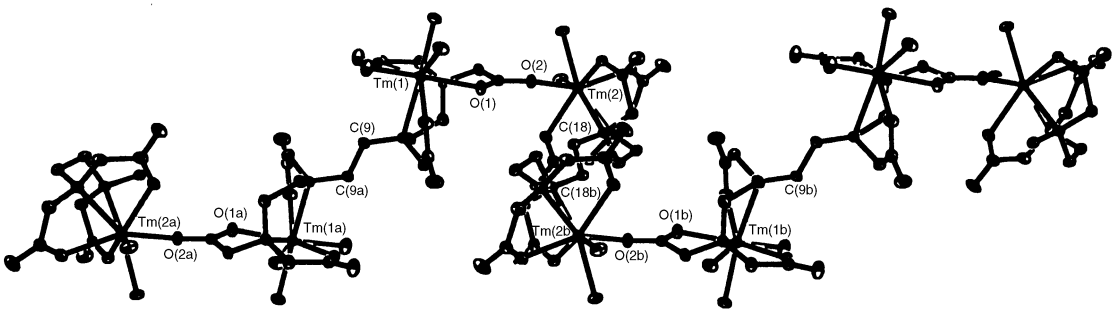

Fig. 2 Chain structure of $\{Tm_2(ttha)(H_2O)_6Tm_2(ttha)(H_2O)_4]\cdot 21H_2O\}_n$ running along crystallographic *c* direction

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References cited in this synopsis

3 C. Paul-Roth and K. N. Raymond, *Inorg. Chem.*, 1995, **34**, 1408.
4 V. Alexander, *Chem. Rev.*, 1995, **95**, 273.
7 R. Y. Wang, J. R. Li, T. Z. Jin, G. X. Xu, Z. Y. Zhou and X. G. Zhou, *Polyhedron*, 1997, **16**, 1361.
8 R. Y. Wang, J. R. Li, T. Z. Jin, G. X. Xu, Z. Y. Zhou and X. G. Zhou, *Polyhedron*, 1997, **16**, 2037.
9 R. Y. Wang, J. R. Li, T. Z. Jin, Z. Y. Zhou and X. G. Zhou, *Chem. Chinese Univ.*, 1999, **20**, in press.
10 R. Ruloff, P. Prokop, J. Sieler, E. Hoyer and L. Beyer, *Z. Naturforsch. Teil B*, 1996, **51**, 963.
11 R. Ruloff, P. Prokop, J. Sieler, E. Hoyer and L. Beyer, *Z. Naturforsch., Teil B*, 1997, **52**, 805.
12 A. Mondry and P. Starynowicz, *Inorg. Chem.*, 1997, **36**, 1176.
13 D. F. Chen, W. C. Yang, R. Y. Wang and T. Z. Jin, *Acta Chim. Sinica*, 1997, **55**, 672.
14 A. Mondry and P. Starynowicz, *J. Chem. Soc., Dalton Trans.*, 1998, 859.
21 J. M. Baker, B. Bleaney, J. S. Brown, C. A. Jr. Hutchion, M. J. M. Leask, P. M. Mortineau, M.R. Wells, J. M. Marin and K. Prout, *J. Magn. Magn. Mater.,* 1983, **31**–**34**, 657.