

Bimetallic Polymeric Macrocyclic Chain Structures Formed by Lanthanide(III) Nitrates and $\text{Hg}(\text{C}_4\text{H}_6\text{NO})_2$; the Crystal Structures of $[\text{Hg}_2\text{Eu}(\text{C}_4\text{H}_6\text{NO})_4(\text{NO}_3)_3]_n$ and $[\text{Hg}_3\text{Tb}_2(\text{C}_4\text{H}_6\text{NO})_6(\text{NO}_3)_6]_n$

David M. L. Goodgame, David J. Williams, and Richard E. P. Winpenny

Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, U.K.

Reaction of HgL_2 ($\text{L} = \text{C}_4\text{H}_6\text{NO}$, the anion of 2-pyrrolidone) with hydrated lanthanide(III) (Ln) nitrates yields two new series of polymeric heterometallic complexes of stoichiometries $\text{Hg}_2\text{LnL}_4(\text{NO}_3)_3$ and $\text{Hg}_3\text{Ln}_2\text{L}_6(\text{NO}_3)_6$, representative members of which [$\text{Ln} = \text{Eu}$ (**1**) and $\text{Ln} = \text{Tb}$ (**2**), respectively] have been structurally characterized.

The exceptional physical properties, especially superconductivity,¹ exhibited by some lanthanide-heterometal oxides make the study of new types of heterometallic polynuclear complexes involving a rare earth ion as one of the metals, potentially both fascinating and rewarding. Such complexes could be useful as precursors for new syntheses of complex metal oxides² or may themselves possess interesting characteristics.³ Recently we have discovered that the anion of 2-pyrrolidone ($\text{C}_4\text{H}_6\text{NO}^-$) is a binucleating ligand which readily binds different metals to form novel polymeric structures.^{4,5} We have now found that this work can be extended to include lanthanides and we report here the crystal structures of two new macrocyclic, bimetallic, chain polymers: $\text{Hg}_2\text{EuL}_4(\text{NO}_3)_3$ (**1**) and $\text{Hg}_3\text{Tb}_2\text{L}_6(\text{NO}_3)_6$ (**2**) (where $\text{L} = \text{C}_4\text{H}_6\text{NO}^-$, the anion of 2-pyrrolidone), which we believe to be representative of the structures formed by lanthanides as a whole.

Reaction of HgL_2 (1 mmol; prepared as described previously⁵) with the appropriate hydrated lanthanide(III) nitrate (0.25 mmol) in methanol (25 cm^3) gave, after three days slow evaporation, small colourless crystals of (**1**) and (**2**).[†] For both compounds the $\nu(\text{CO})$ i.r. band was in the expected region

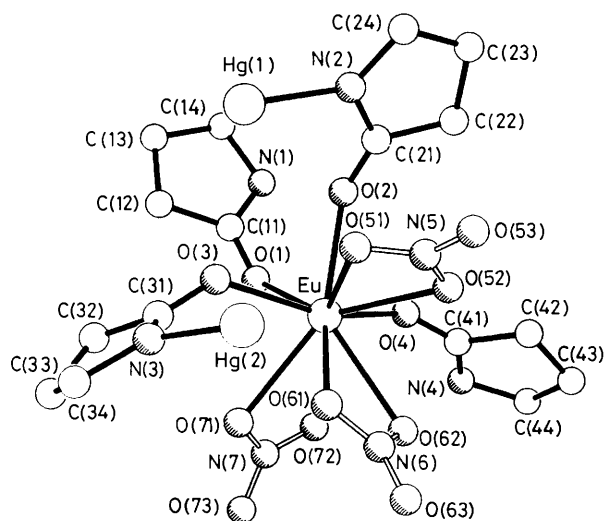


Figure 1. Selected bond lengths (\AA) and angles ($^\circ$) for (**1**): $\text{Eu}-\text{O}(1)$ 2.33, $\text{Eu}-\text{O}(2)$ 2.35, $\text{Eu}-\text{O}(3)$ 2.38, $\text{Eu}-\text{O}(4)$ 2.35, $\text{Eu}-\text{O}(51)$ 2.65, $\text{Eu}-\text{O}(52)$ 2.58, $\text{Eu}-\text{O}(61)$ 2.57, $\text{Eu}-\text{O}(62)$ 2.59, $\text{Eu}-\text{O}(71)$ 2.57; the non-bonded $\text{Eu} \cdots \text{O}(72)$ distance = 2.81 \AA (av. e.s.d. 0.01 \AA); $\text{O}(1)-\text{Eu}-\text{O}(2)$ 72.7, $\text{O}(1)-\text{Eu}-\text{O}(3)$ 79.4, $\text{O}(2)-\text{Eu}-\text{O}(3)$ 85.0, $\text{O}(2)-\text{Eu}-\text{O}(4)$ 78.4, $\text{O}(3)-\text{Eu}-\text{O}(4)$ 156.6, $\text{O}(1)-\text{Eu}-\text{O}(4)$ 80.0 (av. e.s.d. 0.4°).

[(**1**) 1582; (**2**) 1575 cm^{-1}] for 2-pyrrolidone when functioning as a binucleating ligand.⁴

The crystal structures of (**1**) and (**2**) reveal that in both cases the lanthanides (Eu and Tb) are bound to nine oxygen atoms (Figures 1 and 2).[‡] For europium these consist of five nitrate oxygens and four pyrrolidone oxygens, whilst for terbium the division is six and three, respectively. The Ln-O bond lengths are in the usual range for lanthanides though in both cases those from 2-pyrrolidone are significantly shorter [(**1**) ca. 2.35;

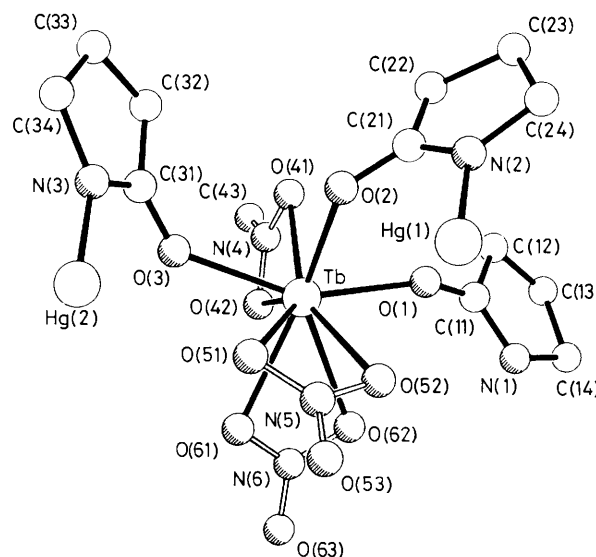


Figure 2. Selected bond lengths (\AA) and angles ($^\circ$) for (**2**): $\text{Tb}-\text{O}(1)$ 2.28, $\text{Tb}-\text{O}(2)$ 2.27, $\text{Tb}-\text{O}(3)$ 2.29, $\text{Tb}-\text{O}(41)$ 2.48, $\text{Tb}-\text{O}(42)$ 2.43, $\text{Tb}-\text{O}(51)$ 2.56, $\text{Tb}-\text{O}(52)$ 2.47, $\text{Tb}-\text{O}(61)$ 2.47, $\text{Tb}-\text{O}(62)$ 2.65 (av. e.s.d. 0.01 \AA); $\text{O}(1)-\text{Tb}-\text{O}(2)$ 79.9, $\text{O}(1)-\text{Tb}-\text{O}(3)$ 152.6, $\text{O}(2)-\text{Tb}-\text{O}(3)$ 83.7 (av. e.s.d. 0.3°).

[‡] Crystal data for (**1**): $\text{C}_{16}\text{H}_{24}\text{Hg}_2\text{EuN}_7\text{O}_{13}$, monoclinic, space group $P2_1/c$, $a = 9.879(2)$, $b = 14.594(3)$, $c = 18.211(3)$ \AA , $\beta = 93.58(2)^\circ$, $U = 2631$ \AA^3 , $Z = 4$, $M = 1075.5$, $D_c = 2.72$ g cm^{-3} , $\mu(\text{Cu}-K\alpha) = 391$ cm^{-1} . For (**2**): $\text{C}_{24}\text{H}_{36}\text{Hg}_3\text{N}_{12}\text{O}_{24}\text{Tb}_2$, monoclinic, space group $P2_1/c$, $a = 11.833(4)$, $b = 13.070(2)$, $c = 14.435(3)$ \AA , $\beta = 98.65(2)^\circ$, $U = 2207$ \AA^3 , $Z = 2$, $M = 1796.2$, $D_c = 2.71$ g cm^{-3} , $\mu(\text{Cu}-K\alpha) = 360$ cm^{-1} . Data for both compounds were measured on a Nicolet R3m diffractometer with graphite-monochromated $\text{Cu}-K\alpha$ radiation using ω -scans. Both structures were solved by the heavy-atom method and refined anisotropically using absorption corrected data to give for (**1**) $R = 0.046$, $R_w = 0.044$ for 2707 independent observed reflections; for (**2**) $R = 0.036$, $R_w = 0.035$ for 2282 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leq 58^\circ$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[†] Satisfactory microanalytical results were obtained for all the compounds reported here.

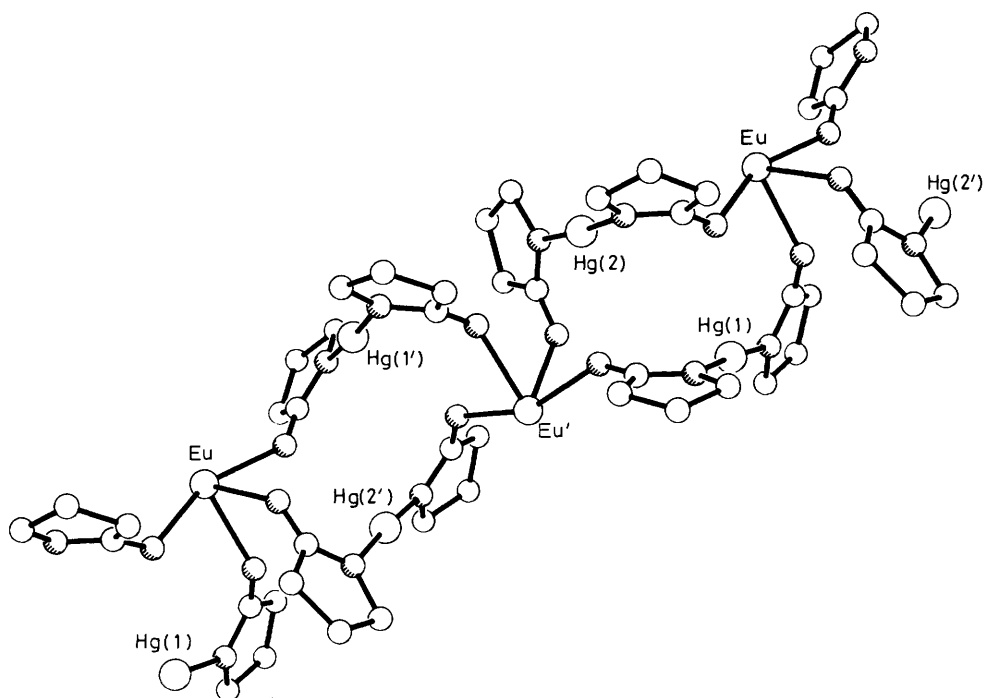


Figure 3. Part of the polymeric chain structure of (1) showing the interlocking 16-membered rings. The NO_3 groups have been omitted for clarity.

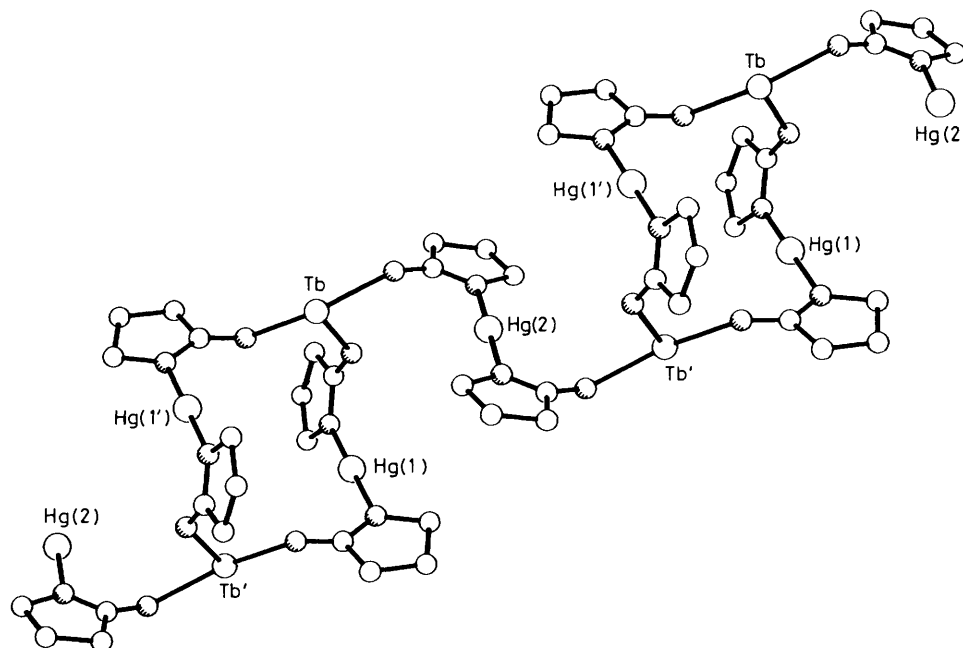


Figure 4. Part of the polymeric chain structure of (2) showing the alternating 16-membered macrocycles with Hg_2L_2 links. The NO_3 groups have been omitted for clarity.

(2) *ca.* 2.28 Å] than those from nitrate [(1) *ca.* 2.59; (2) *ca.* 2.53 Å], as expected. §

In both compounds, the mercury atoms form essentially linear [(1) 176.4(4) and 175.6(5); (2) 178.6(3) and 180°] bonds to two pyrrolidone nitrogens [Hg–N (1) *ca.* 2.04; (2) *ca.* 2.02 Å].

§ *E.g.* in $\text{Nd}(\text{NO}_3)_3(\text{C}_{11}\text{H}_{12}\text{ON}_2)_3$ (where $\text{C}_{11}\text{H}_{12}\text{ON}_2$ is antipyrine) Nd–O(nitrate) 2.54, Nd–O(antipyrine) 2.34 Å.⁷

The subtle change observed in the co-ordination sphere of the lanthanide ion on changing from Eu to Tb (presumably caused by the smaller ionic radius of Tb^{3+}) leads to a considerable change in the overall polymeric structure. ¶ In (1) a chain polymer made up of interlocking 16-membered macrocyclic links is formed (Figure 3), whilst in (2) the

¶ *N.b.* Changes of the molar ratios of the reactants still afforded in each case the same product stoichiometries.

polymer consists of similar 16-membered rings although with alternating HgL_2 linking units (Figure 4). The macrocycles, although similarly constituted, do not have identical dimensions, with the ring in (1) more elongated than that in (2) [Eu–Eu 7.6, cf. Tb–Tb 7.1 Å]. The elongation of the Eu–Eu distance in (1) is accompanied by a corresponding Hg–Hg contraction [Hg(1)–Hg(2) in (1) 4.45, Hg(1)–Hg(1') in (2) 5.13 Å]. The macrocyclic links that constitute the Eu structure are reminiscent of those formed in the analogous Co structure, although with the transannular HgL_2 strut removed.⁵ With Tb this additional strut is retained but serves, as stated above, to link adjacent macrocycles rather than create the macrobicyclic units present in the Co structure. In both cases these structures are in striking contrast to the contiguous 32-membered macrocyclic arrays formed with Cu.⁴

In both compounds the polymers run along the crystallographic *b* axis direction. Structure-stabilising inter-polymer interactions are more important here than in previously reported bimetallic complexes of 2-pyrrolidone.^{4,5} These interactions are chiefly between nitrate oxygens in one strand and mercury atoms in the next. Nearest contacts are: (1) O(63)–Hg(2) 2.95 and O(73)–Hg(1) 2.96; (2) O(63)–Hg(2) 2.93 and O(63)–Hg(1) 3.28 Å.

X-Ray powder diffraction studies indicate that the analogous complexes formed with the lanthanides, from lanthanum to gadolinium (promethium not studied) are isostructural with (1), whilst those with yttrium and the lanthanides from terbium to ytterbium form a series isostructural with (2). These observations support the proposition that the structural

change is due to a change in the ionic radius of the lanthanide ion.

The novelty and diversity of the structural types so far exhibited by the polynuclear complexes formed by the $\text{Hg}(\text{C}_4\text{H}_6\text{NO})_2$ unit both with transition metals^{4,5} and lanthanide ions may be attributed to the particular combinations of the differing preferred donor sets and co-ordination geometries of the heterometal atoms employed. Development of this approach by appropriate choices of the organic bridge and the heterometal ions appears to be a potentially fruitful source of further new types of extended structure.

We thank the S.E.R.C. for a studentship (to R.E.P.W.).

Received, 30th November 1987; Com. 1732

References

- 1 A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 579.
- 2 C. N. R. Rao and J. Gopalakrishnan, *Acc. Chem. Res.*, 1987, **20**, 228.
- 3 C. Shan, Y. Lin, J. Ouyang, Y. Fan, and G. Yang, *Makromol. Chem.*, 1987, **188**, 629.
- 4 D. M. L. Goodgame, D. J. Williams, and R. E. P. Winpenny, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1044.
- 5 D. M. L. Goodgame, D. J. Williams, and R. E. P. Winpenny, *Angew., Chem., Int. Ed. Engl.*, in the press.
- 6 S. P. Sinha, *Struct. Bonding (Berlin)*, 1976, **25**, 69.
- 7 K. K. Bhandary and H. Marokar, *Acta Crystallogr., Sect. B*, 1976, **32**, 861.