Formation of a Heterometallic (Hg–Gd) Polymeric Complex of 2-Oxazolidone consisting of Fused 16- and 48-membered Macrocyclic Rings; Crystal Structure of $[Hg_2(C_3H_4NO_2)_4Gd(NO_3)_3]_n$

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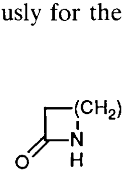
2-Oxazolidone (LH = $C_3H_5NO_2$) reacts with mercury(II) acetate and gadolinium(III) nitrate in methanol to form the polymeric complex $[Hg_2(C_3H_4NO_2)_4Gd(NO_3)_3]_n$ which consists of a unique array of contiguous 16- and 48-membered macrocycles.

Lactam rings of general formula **I** have proved to be remarkably versatile in their ability to generate polymeric Hg–M heterometallic compounds containing macrocyclic rings incorporating the metal atoms as part of the ring framework.[1] The sizes of the metallamacrocycles that result, and the ways in which these link to form chains, sheets or three-dimensionally linked networks, depend on the nature of the metal ion, M, accompanying the mercury, and on the lactam ring size.

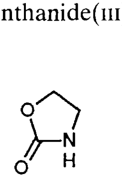
To explore the effect of incorporating a further potential donor atom within the ring system of the organic ligand we have investigated the use of 2-oxazolidone **II**. The presence in this ligand of two oxygen atoms, as opposed to one in the lactam rings, offers the opportunity of alternative modes of binding to the metal M (especially in the case of lanthanide ions) and hence of modifying the nature of any macrocyclic/polymeric arrays created. Use of **II** as the bridging ligand and the synthetic method previously employed with 2-pyrrolidone (**I**, n = 2) has afforded colourless crystals of a mercury–gadolinium complex of stoichiometry $Hg_2(C_3H_4NO_2)_4Gd(NO_3)_3 \cdot MeOH$ **1**.

Although, with lactams, a wide variety of macrocycle ring sizes has been obtained (8-,[2] 16-,[3] 32-,[4] 48-[1] and 80-membered[2a] systems) we have not, hitherto, observed any examples containing more than one size of these macrocycles in the same polymeric array. X-Ray diffraction analysis† of **1**, however, shows that this new compound forms a most unusual polymeric array consisting of fused 16- and 48-membered rings.

In **1** the gadolinium atom is nine-coordinate, being bonded to carbonyl oxygen atoms from four oxazolidone rings and oxygen atoms from two bidentate nitrates and one monodentate nitrate (Fig. 1). The Gd–O distances lie in two groups, those to the carbonyl oxygen atoms being in the range 2.32–2.41(1) Å and those to nitrate oxygens in the range 2.43–2.56(1) Å, the shortest of the latter being to the oxygen atom of the monodentate nitrate group. The coordination geometry about the gadolinium atom is best described as tricapped trigonal prismatic, a geometry that we have observed previously for the mercury–lanthanide(III) complexes with 2-pyrrolidone.[3] The ring oxygen atom of the 2-oxazolidone ligand is not involved in any significant intra- or inter-molecular interactions.‡ Each mercury atom is linked to a pair of oxazolidone nitrogen atoms in a near linear arrangement [177.7(5)° at Hg(1) and 176.9(5)° at Hg(2), with N–Hg distances in the range 2.00(1)–2.04(1) Å].



I



II

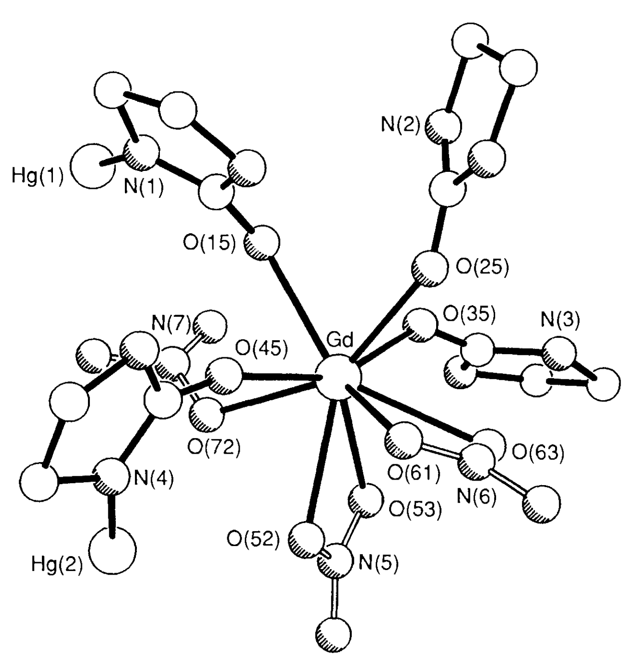


Fig. 1 The nine-coordinate arrangement about the gadolinium atom in **1** with selected bond lengths (Å): Gd–O(15) 2.407(9), Gd–O(25) 2.362(10), Gd–O(35) 2.361(9), Gd–O(45) 2.324(10), Gd–O(52) 2.513(9), Gd–O(53) 2.553(11), Gd–O(61) 2.560(13), Gd–O(63) 2.511(11), Gd–O(72) 2.426(12)

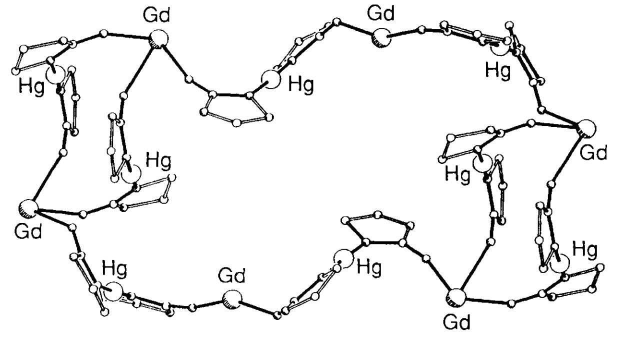


Fig. 2 Part of the contiguous array of fused 16- and 48-membered rings. The periphery of each macrocycle is emphasized with bold lines.

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† *Crystal data* for **1**: $Hg_2(C_3H_4NO_2)_4Gd(NO_3)_3 \cdot MeOH$, M = 1120.8, monoclinic, a = 10.110(4), b = 18.494(5), c = 13.952(4) Å, β = 99.80(3)°, U = 2570 Å^3, space group $P2_1/n$, Z = 4, D_c = 2.90 g cm^{-3}, μ(Cu-Kα) = 409 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.049, R_w = 0.047 for 3033 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ The included methanol solvent molecule does not play any significant role in the structure; it is oriented such that both partial occupancy oxygen atoms make a near orthogonal approach (O–Hg *ca.* 2.7 Å) to one of the pair of N–Hg–N units.

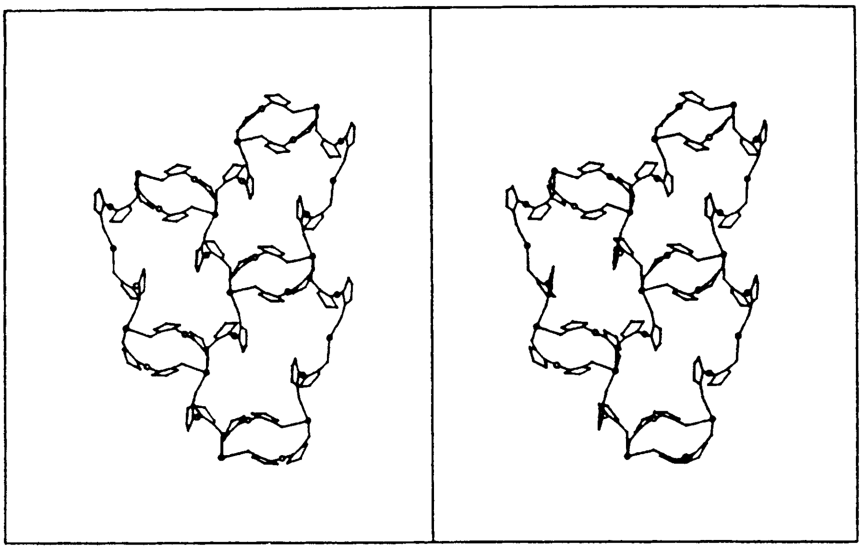

Fig. 3 Stereoscopic representation of part of the polymeric array formed by **1** in the crystal

The fascinating feature of the structure is the nature of the polymeric array that is formed as a consequence of the linking of adjacent gadolinium centres *via* the L–Hg–L bridges. Hitherto, where the lanthanide ion is coordinated to four pyrrolidone (pyrr) ligands a chain polymer is formed,[3] in which the basic repeat unit consists of 16-membered $M_2Hg_2(pyrr)_4$ rings. Here, use of **II**, which has the same ligand ring size and utilizes the same donor atoms as 2-pyrrolidone, results in a dramatic change in the overall structure. As previously, two of the organic ligands bridge *via* the mercury atom to an adjacent centrosymmetrically related gadolinium centre forming a 16-membered ring. The other two, however, bridge *via* a glide-related gadolinium centre to another, lattice-translated gadolinium atom, creating a 48-membered centrosymmetric macrocycle (consisting of six gadolinium, six mercury, twelve carbon, twelve nitrogen and twelve oxygen atoms).

Thus, for the first time, we have the coexistence of both 16- and 48-membered macrocycles, each with a common edge (Fig. 2). The nature of the contiguous, sinuous array thus created can best be seen in the stereoscopic drawing of the structure (Fig. 3; from which the nitrate ligands, which are directed in towards the centre of the 48-membered macrocycle, have been omitted for clarity).

The dramatically different structure found for the apparently analogous pair of compounds $[Hg_2L_4Gd(NO_3)_3]_n$ on changing L from 2-pyrrolidone[3] to the closely related ligand 2-oxazolidone provides a striking example of the structural versatility of this family of new compounds.

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