Metallation of β-Propiolactam; Crystal Structures of $Hg(C_3H_4NO)_2 \cdot H_2O$ and of the Bimetallic Polymeric 48-Membered Macrocyclic Complex $[Hg_3(C_3H_4NO)_6Er_2(NO_3)_6]_n$

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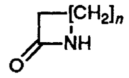
β-Propiolactam (LH = C_3H_5NO) is shown to be metallated at the nitrogen atom to form the complex $HgL_2 \cdot H_2O$ (**1**) and, in the presence of both mercury(II) and erbium(III) ions, to form a polymeric, 48-membered, puckered macrocyclic array $[Hg_3(L)_6Er_2(NO_3)_6]_n$ (**2**).

Although the β-propiolactam ring is a component of many pharmacologically important drugs, convenient, high-yielding syntheses[1,2] of the parent ring (**Ia**) and its detailed molecular structure[3] have only recently been reported. In common with its higher homologues (**I**, n = 2, 3, 4), (**Ia**) offers the potential not only for metallation at the ring nitrogen by proton displacement but also to bind further metals *via* its carbonyl oxygen atom. Such studies have opened up a fascinating new family of novel polymeric, bimetallic compounds with a wide range of metals.[4] We report here the synthesis and structural characterisation of what we believe to be the first metal complexes of (**Ia**) (= LH), *viz.* $HgL_2 \cdot H_2O$ (**1**) and $[Hg_3(L)_6Er_2(NO_3)_6]_n$ (**2**).

Evaporation of a methanol solution of (**Ia**) and mercury(II) acetate in 2 : 1 mole ratio gave a white glassy solid, which afforded (**1**) as thin colourless plates on recrystallisation from acetonitrile. Pale pink crystals of (**2**) separated overnight from methanol solutions of (**Ia**), mercury(II) acetate, and hydrated erbium(III) nitrate in 4 : 2 : 1 mole ratio.



(I)

a; n = 1
b; n = 2

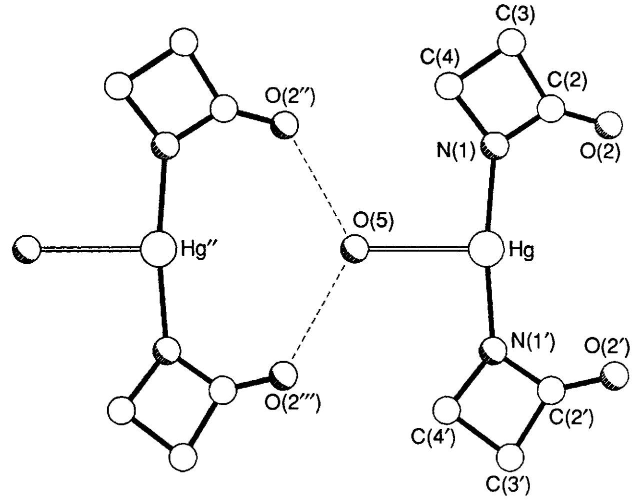


Figure 1. Part of the hydrogen-bonded $HgL_2{\cdot}H_2O$ chains, showing the atom numbering.

The *X*-ray study† shows (Figure 1) that (**1**) has the stoicheiometry $HgL_2{\cdot}H_2O$. The mercury atom is bound to (**Ia**) *via* the nitrogen atom [Hg–N 2.011(11) Å]. The complex has crystallographic C_2 symmetry, with the two β-lactam rings rotated respectively by *ca.* 22° about the N–N′ vector. Each β-lactam ring is planar (to within 0.007 Å) and has a geometry that matches, within the limits of accuracy of this determination, that of the uncomplexed ring.[3] There is a marginal, though not statistically significant, increase in the N(1)–C(2) bond length, possibly reflecting the influence of metallation at the nitrogen atom.

The water molecule forms an integral part of this structure. It lies on the two-fold axis and adjacent to the mercury atom at a distance of 2.59(2) Å. This results in a slight deformation of the N–Hg–N′ linkage [N–Hg–N′ angle 171.6(5)°]. The water molecule also forms hydrogen bonds (2.83 Å) to the carbonyl oxygen atoms of lattice-translated HgL_2 units along the two-fold axis, producing a hydrogen-bonded chain structure. The $[HgL_2{\cdot}H_2O]_n$ sheets stack (interplanar separation 3.3 Å) with adjacent sheets being displaced such that the carbonyl oxygen atoms in one sheet are positioned above and at a distance of 3.0 Å from the mercury atoms of the next.

The *X*-ray structure analysis† of (**2**) shows (Figure 2) the complex to have the stoicheiometry $Hg_3(L)_6Er_2(NO_3)_6$. The erbium atom is nine-co-ordinate, being bonded to three β-lactam oxygen atoms and six oxygen atoms from three bidentate nitrate groups. This stoicheiometry is the same as that found for the 2-pyrrolidone (**Ib**) complexes of the lanthanides Tb to Yb,[5] with, as in the case of the Tb complex, one HgL_2 unit lying on a centre of symmetry and the other in a general position. However, although, in (**2**), adjacent lanthanide centres are again linked *via* the HgL_2 units, the resulting polymeric array is totally different from any we have previously observed. Whereas the mercury/lanthanide complexes formed by (**Ib**) produced chain polymers, here contiguous, macrocyclic, polymeric sheets result (Figure 3). The basic unit within each sheet is a 48-membered ring consisting of six erbium, six mercury, twelve carbon, twelve nitrogen, and twelve oxygen atoms. Each of these chains has a pronounced sinusoidal nature, producing a corrugated array for each sheet. There are no short transannular metal–metal contacts; all are greater than 4 Å.

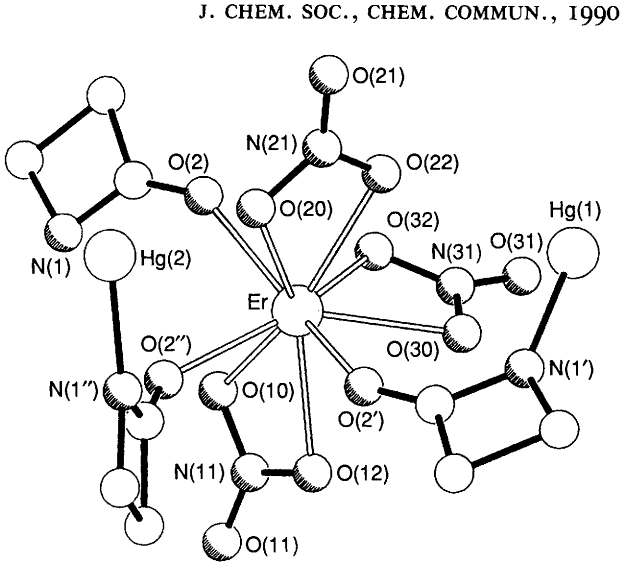


Figure 2. The environment around the Er atom in (**2**) with selected bond lengths (Å): Er–O(2) 2.249(5), Er–O(2′) 2.284(6), Er–O(2″) 2.277(5), Er–O(10) 2.456(6), Er–O(12) 2.415(7), Er–O(20) 2.473(6), Er–O(22) 2.394(6), Er–O(30) 2.452(6), Er–O(32) 2.447(8), Hg(1)–N(1′) 2.014(8), Hg(2)–N(1″) 2.027(7), Hg(1)–N(1*) 2.025(7) [linking to N(1) on adjacent Er centre].

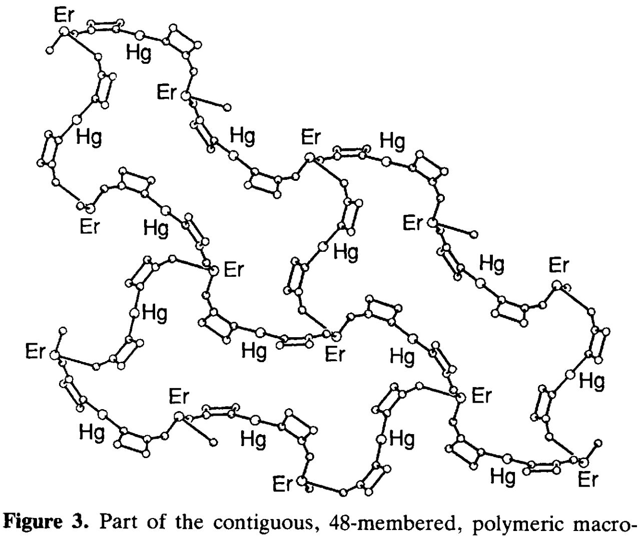


Figure 3. Part of the contiguous, 48-membered, polymeric macrocyclic array of (**2**). The NO_3 groups have been omitted for clarity.

The differences in macrocycle size and geometry compared with those formed by (**Ib**) are almost certainly due to the differences in ligand ‘bite.’ Despite metal co-ordination at both ring nitrogen and carbonyl oxygen atoms the overall

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† *Crystal Data* for (**1**): $C_6H_8N_2O_2Hg{\cdot}H_2O$, $M = 358.7$, monoclinic, space group $C2/c$, $a = 8.515(3)$, $b = 6.434(2)$, $c = 16.239(7)$ Å, $\beta = 106.92(3)°$, $U = 851$ Å^3, $Z = 4$ (the molecule is disposed about a 2-fold axis), $D_c = 2.80$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 347$ cm^{-1}. For (**2**): $C_{18}H_{24}Er_2Hg_3N_{12}O_{24}$, $M = 1728.7$, monoclinic, space group $P2_1/n$, $a = 9.196(4)$, $b = 15.118(5)$, $c = 14.326(5)$ Å, $\beta = 101.02(3)°$, $U = 1955$ Å^3, $Z = 2$ (the molecule is disposed about a centre of symmetry), $D_c = 2.94$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 308$ cm^{-1}. Data for both compounds were measured on a Nicolet R3m diffractometer with graphite-monochromated Cu-K_α radiation using ω-scans. Both structures were solved by the heavy atom method and refined anisotropically using absorption-corrected data to give for (**1**) $R = 0.037$, $R_w = 0.041$ for 574 independent observed reflections; for (**2**) $R = 0.032$, $R_w = 0.037$ for 2520 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leqslant 116°$]. 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.

geometries of the three independent β-lactam units are all essentially the same as that in the parent ligand. Furthermore, in both structures metallation does not result in any significant pyramidality at the nitrogen atom; a planar geometry comparable to that in the uncomplexed ligand[3] is retained.

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