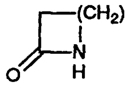
Synthesis and X-Ray Characterisation of Some Heterometallic Hg–M Complexes with 2-Oxazolidone[†]

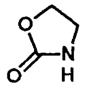
Louisa H. Carrad, David M. L. Goodgame,* Stuart P. W. Hill and David J. Williams
Chemistry Department, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

Mercury(II) acetate reacts with 2-oxazolidone (1,3-oxazolidin-2-one, $C_3H_5NO_2$) in methanol to produce $[HgL_2]$ (L = $C_3H_4NO_2$, the anion of 2-oxazolidone). An X-ray diffraction study has shown that the Hg atom binds to the ring nitrogen atom with a near linear N–Hg–N geometry. There are two HgL_2 groups in the asymmetric unit which are orthogonal to one another and linked *via* pairs of Hg ··· O interactions to form dimers. These bind to neighbouring units *via* weaker Hg–O interactions to form a one-dimensional chain polymer. When yttrium or lanthanide(III) nitrates are added to the reaction an isostructural series of compounds of formula $[\{Hg_2L_4M(NO_3)_3\}_n]$, where M = La–Yb or Y, is obtained. A representative member of this group, $[\{Hg_2L_4Gd(NO_3)_3\}_n]$, was studied by single-crystal X-ray diffraction methods. This forms a two-dimensional polymeric array comprising two sizes of metallamacrocyclic rings (16- and 48-membered) fused together, with the gadolinium(III) ion surrounded by nine oxygen atoms in a trigonal tricapped-prismatic arrangement. The IR, UV/VIS reflectance, EPR and solid-state NMR spectroscopic properties of these complexes and, where appropriate, those of $[Hg_3L_6Co(NO_3)_2]$ and $[Hg_2L_4Zn(NO_3)_{1.33}(OMe)_{0.67}]$ are reported.

We have shown that lactam rings of general formula **I** are very versatile in producing a wide range of cyclic Hg–M complexes in which the metal atoms form an integral part of the metallamacrocyclic frameworks. The sizes of the rings formed (8-,[1-3] 12-,[3] 16-,[4] 32-,[5] 48-,[6] or 80-membered[1a]) seem to depend on two factors, the nature of the metal ion, M, accompanying the mercury, and the lactam ring size.



I



II

In view of the variety of results obtained with 2-pyrrolidone **I** (n = 2)[1,4,5] it was decided to keep the lactam ring size the same and to investigate the effect of replacing the methylene group adjacent to the carbonyl by an oxygen atom as in 2-oxazolidone (1,3-oxazolidin-2-one) **II**. As oxygen is more electronegative, this has the potential of inducing electronic changes and thus altering the binding properties of the nitrogen atom and the exocyclic oxygen as well as providing an additional potential binding site for a 'hard' metal ion.

Reaction of mercury(II) acetate, silver(I) nitrate and **II** resulted in the complex $[\{Hg(C_3H_4NO_2)_2Ag(NO_3)\}_n]$ which has an overall structure[3] similar to that of the analogous 2-pyrrolidone compound,[1b] but with some subtle differences. For instance, in the 2-pyrrolidone compound the central feature is an Ag_4O_4 cubane-like species, whereas in the 2-oxazolidone case the Ag_4O_4 unit is sheared, forming a 'step' species.[3]

Due to the current interest in new heterometallic solid-state materials involving yttrium and f-block elements, we have explored the preparation and properties of related compounds formed by $[Hg(C_3H_4NO_2)_2]$ with yttrium(III) and lanthanide(III) metal ions. We report here the results of our synthetic, structural and spectroscopic studies on these complexes and on some related Co^{II}–Hg and Zn^{II}–Hg compounds. A brief account of some of these results has been given in a preliminary communication.[7] We have also investigated the geometry and structure of the 'parent' $[HgL_2]$ (L = $C_3H_4NO_2$) compound by X-ray analysis.

Experimental

Preparation of Compounds.—The compound $[Hg(C_3H_4NO_2)_2]$ **1** was prepared by dissolving mercury(II) acetate (0.1 mmol) and 2-oxazolidone (0.2 mmol) in methanol (10 cm^3). The resultant solution was allowed to stand at room temperature over concentrated sulfuric acid. After 4 d, colourless needles suitable for X-ray structural analysis started to form.

The lanthanide mercury 2-oxazolidone complexes **2**–**13** (see Table 1) were prepared by dissolving mercury(II) acetate (0.1 mmol), 2-oxazolidone (0.2 mmol) and the appropriate metal nitrate (0.06 mmol) in methanol (14 cm^3) and allowing the mixture to stand over concentrated sulfuric acid at room temperature for several days. The use of methanol (*ca.* 14 cm^3) gave the compounds in good crystalline form; powders were formed if less methanol was used. The gadolinium(III)-doped compounds were prepared by an identical procedure, with the addition of *ca.* 1 mol% $Gd(NO_3)_3 \cdot 5H_2O$ to the reaction solution.

Compounds **14** and **15** were prepared by mixing mercury(II) acetate (0.1 mmol), 2-oxazolidone (0.2 mmol) and then respectively either hydrated cobalt(II) nitrate (0.5 mmol), or zinc(II) nitrate (0.15 mmol) in methanol (10 cm^3). Each mixture was left at room temperature over concentrated sulfuric acid. Compound **14** separated as a pink powder after 3 d, while **15** produced a white powder after 5 d (sometimes contaminated with HgL_2, especially in low dilution of methanol).

Analytical data (Microanalytical Laboratory, Imperial College) are given in Table 1.

Spectroscopy.—Infrared spectra were recorded on a Perkin Elmer 1720 FT spectrometer as Nujol mulls (KBr or CsI) in the range 220–4000 cm^{-1}. Compounds **2**–**13** showed nitrate ν(NO) bands at 1485, 1436, 1332, 1312, 1017 cm^{-1} (in each case ±2

[†] *Supplementary data available* (No. SUP 56931, 4 pp.): electronic and EPR spectral data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Yields and analytical data for the compounds

Complex	Yield (%)	Product	Microanalysis (%)* C	H	N
1 $[Hg(C_3H_4NO_2)_2]$	74	Colourless needles	19.3 (19.3)	2.0 (2.1)	7.4 (7.5)
2 $[Hg_2(C_3H_4NO_2)_4La(NO_3)_3]$	90	Rhombic colourless crystals	13.4 (13.5)	1.6 (1.5)	8.6 (9.2)
3 $[Hg_2(C_3H_4NO_2)_4Ce(NO_3)_3]$	87	White microcrystals	13.3 (13.4)	1.5 (1.5)	8.9 (9.1)
4 $[Hg_2(C_3H_4NO_2)_4Pr(NO_3)_3]\cdot MeOH$	84	Pale green microcrystals	13.9 (14.1)	1.6 (1.8)	8.9 (8.9)
5 $[Hg_2(C_3H_4NO_2)_4Nd(NO_3)_3]\cdot MeOH$	80	Lilac-purple needles	14.0 (14.1)	1.6 (1.8)	8.7 (8.8)
6 $[Hg_2(C_3H_4NO_2)_4Sm(NO_3)_3]\cdot MeOH$	78	White microcrystals	13.7 (14.0)	1.6 (1.8)	8.4 (8.8)
7 $[Hg_2(C_3H_4NO_2)_4Eu(NO_3)_3]$	70	White powder	13.3 (13.3)	1.5 (1.5)	8.8 (9.0)
8 $[Hg_2(C_3H_4NO_2)_4Gd(NO_3)_3]\cdot MeOH$	75	Colourless needles	14.0 (13.9)	1.6 (1.8)	8.9 (8.7)
9 $[Hg_2(C_3H_4NO_2)_4Tb(NO_3)_3]$	70	Colourless microcrystals	13.0 (13.2)	1.4 (1.5)	8.6 (9.0)
10 $[Hg_2(C_3H_4NO_2)_4Dy(NO_3)_3]\cdot MeOH$	66	Colourless needles	13.9 (13.8)	1.7 (1.8)	8.5 (8.7)
11 $[Hg_2(C_3H_4NO_2)_4Ho(NO_3)_3]$	79	Salmon-pink needles	13.1 (13.1)	1.4 (1.5)	8.4 (8.9)
12 $[Hg_2(C_3H_4NO_2)_4Er(NO_3)_3]\cdot MeOH$	86	Pink needles	13.5 (13.8)	1.5 (1.5)	8.6 (8.7)
13 $[Hg_2(C_3H_4NO_2)_4Y(NO_3)_3]\cdot MeOH$	70	Colourless needles	14.6 (14.8)	1.7 (1.9)	9.4 (9.3)
14 $[Hg_3(C_3H_4NO_2)_6Co(NO_3)_2]$	80	Pink powder	16.4 (16.6)	1.6 (1.8)	8.3 (8.6)
15 $[Hg_2(C_3H_4NO_2)_4Zn(NO_3)_{1.33}(OMe)_{0.67}]$	78	White powder	16.7 (16.6)	1.8 (1.9)	8.4 (8.2)

* Calculated results in parentheses.

cm^{-1}) and a pair of sharp bands at 817–830 cm^{-1} in the O–N–O out-of-plane deformation region. The UV/VIS reflectance spectra were recorded on a Beckman DK2 spectrophotometer on polycrystalline samples in the range 4000–30 000 cm^{-1}. A Perkin Elmer LS50 luminescence spectrometer fitted with the standard solid-state sample accessory was used to obtain the luminescence spectra. The EPR spectra were measured at room temperature on polycrystalline samples using a Q-band spectrometer comprising a Varian 36-GHz microwave bridge and a Newport 12-in type F magnet powered by a C905 rotary generator and post stabiliser. Solid-state ^{13}C NMR spectra were recorded on a Bruker MSL-300 multinuclear spectrometer with cross-polarisation (CP) and magic angle spinning (MAS). X-Ray powder diffraction experiments were carried out on a Guinier focusing camera using Cu-Kα radiation. Single-crystal unit cell dimensions were obtained from oscillation and Weissenberg photographs using Cu-Kα radiation.

Crystallography.—Crystal data. $[\{Hg(C_3H_4NO_2)_2\}_2]$ **1**, $C_{12}H_{16}Hg_2N_4O_8$, $M = 745.5$, monoclinic, space group $P2_1/c$, $a = 10.644(2)$, $b = 9.350(1)$, $c = 17.239(4)$ Å, $\beta = 95.53(2)°$, $U = 1708$ Å^3, $Z = 4$, $D_c = 2.90$ g cm^{-3}, μ(Cu-Kα) = 347 cm^{-1}, $\lambda = 1.541\ 78$ Å, $F(000) = 1360$. Colourless, air-stable needles, crystal dimensions 0.03 × 0.16 × 0.20 mm.

$[Hg_2(C_3H_4NO_2)_4Gd(NO_3)_3]\cdot MeOH$ **8**, $C_{13}H_{20}GdHg_2N_7O_{18}$, $M = 1120.8$, monoclinic, space group $P2_1/n$, $a = 10.110(4)$, $b = 18.494(5)$, $c = 13.952(4)$ Å, $\beta = 99.80(3)°$, $U = 2570$ Å^3, $Z = 4$, $D_c = 2.90$ g cm^{-3}, μ(Cu-Kα) = 409 cm^{-1}, $\lambda = 1.541\ 78$ Å, $F(000) = 2059$. Colourless, air-stable needles, crystal dimensions 0.06 × 0.10 × 0.16 mm.

Data collection and processing. Nicolet R3m diffractometer, ω-scan method ($2\theta < 116°$), graphite-monochromated Cu-Kα radiation. For compounds **1** and **8** 2281 and 3455 unique reflections were measured; 2000 and 3033, respectively, were considered observed $[|F_o| > 3\sigma(|F_o|)]$, corrected for Lorentz and polarisation factors. Numerical absorption corrections (face-indexed crystal) were applied, minimum and maximum transmission factors being 0.055 and 0.389 for **1** and 0.030 and 0.187 for **8**.

Structure analysis and refinement. Both structures were solved by the heavy-atom method and the non-hydrogen atoms refined anisotropically. For **8** a ΔF map revealed the presence of two 50% occupancy methanol molecules of solvation. The positions of the hydrogen atoms were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2\ U_{eq}(C)$, and allowed to ride on their parent carbon atoms. The hydrogen atoms of the partial-occupancy methanol molecules could not be isolated. Refinement was by block-cascade full-matrix least squares to give: for **1**, $R = 0.041$, $R' = 0.043$ $[w^{-1} = \sigma^2(F) + 0.000\ 65F^2]$; for **8**, $R = 0.049$, $R' = 0.047$ $[w^{-1} = \sigma^2(F) + 0.000\ 70F^2]$. The maximum and minimum residual electron densities in the final ΔF maps were: for **1**, 1.54 and −1.54 e Å^{-3}; for **8**, 1.56 and −2.15 e Å^{-3}. The mean and maximum shift/error in the final refinements were: for **1**, 0.012 and 0.066; for **8**, 0.003 and 0.018. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system[8] and published scattering factors.[9] Atomic coordinates for compounds **1** and **8** are listed in Tables 2 and 3, and important bond lengths and angles for both **1** and **8** in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles for both compounds.

Results and Discussion

Reaction of mercury(II) acetate and 2-oxazolidone in methanol readily gave colourless needles of the compound $[Hg(C_3H_4NO_2)_2]$ **1** in good yield. The same procedure using ternary mixtures of mercury(II) acetate, 2-oxazolidone, and the hydrated nitrates of yttrium and the lanthanide(III) ions from La to Er (excluding Pm) also afforded good yields of complexes of stoichiometry $Hg_2L_4Ln(NO_3)_3$. These, when in good crystalline form and not subjected to strong drying, formed as methanol solvates. Attempts to prepare the analogous complexes with Ln = Tm or Yb always resulted in samples which, from analytical data and X-ray powder diffraction studies, were mixtures of the relevant $Hg_2L_4Ln(NO_3)_3$ complex and $[HgL_2]$. The constancy of the stoichiometry $Hg_2L_4Ln(NO_3)_3$ across the lanthanide series contrasts with the behaviour found[4b] with 2-pyrrolidone, where only La to Gd has this stoichiometry, whereas yttrium and Tb to Yb have the formula $Hg_3L_6Ln_2(NO_3)_6$.

Attempts to form other Hg–M heterometallic complexes with **II** were much less successful than had been found previously for 2-pyrrolidone. Hydrated nitrates of Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn, and Cd were used, but heterometallic complexes were obtained only for cobalt(II) (compound **14**) and zinc (compound **15**). With the other metal ions the 'parent' $[HgL_2]$ complex **1** appeared to be preferentially formed, and some preparations of **15** gave samples contaminated with **1**. The partial replacement of nitrate ions by methoxide ions in **15** parallels a corresponding solvolysis in the solid zinc complex formed by 2-pyrrolidone.[1a]

Structure of $[Hg(C_3H_4NO_2)_2]$ **1**.—The X-ray analysis

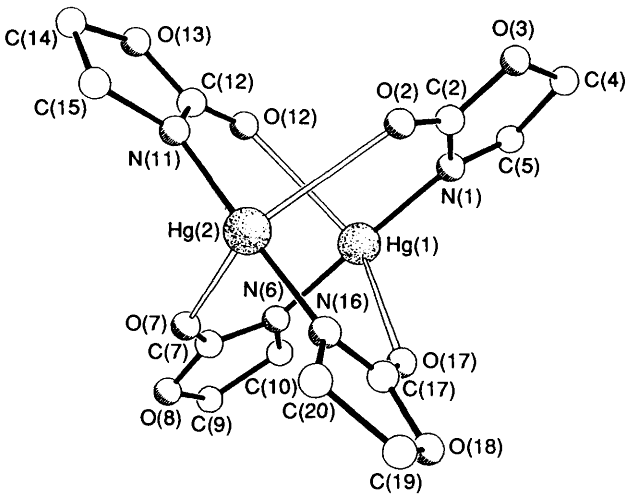


Fig. 1 Linked pairs of HgL_2 molecules that comprise the dimeric asymmetric unit in the structure of complex **1**

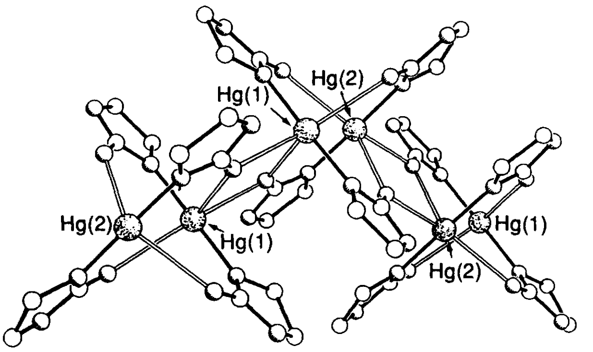


Fig. 2 Part of the oxygen-bridged polymeric chain in the structure of complex **1**

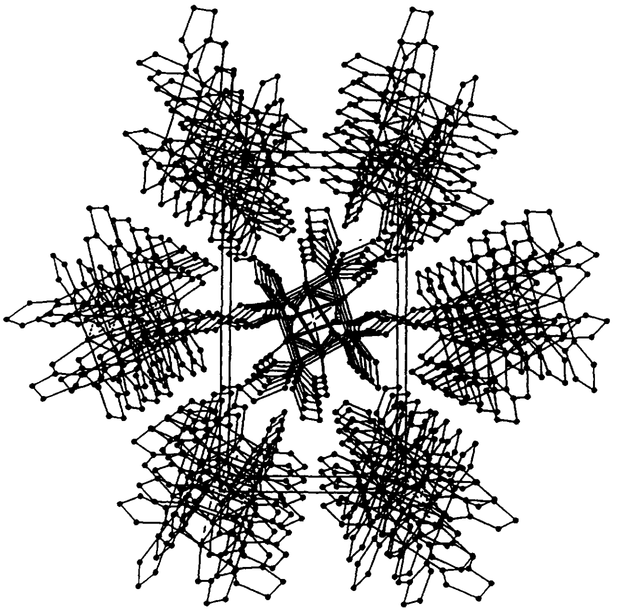


Fig. 3 The close-packed hexagonal array of the polymeric chains in the structure of complex **1** viewed down the *a* direction

Table 2 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Hg(1)	1201(1)	413(1)	940(1)
N(1)	535(10)	−1292(10)	1492(7)
C(2)	1099(14)	−2573(14)	1481(8)
O(2)	2109(9)	−2891(10)	1253(7)
O(3)	362(10)	−3584(10)	1796(7)
C(4)	−691(16)	−2887(16)	2109(11)
C(5)	−708(13)	−1374(14)	1762(10)
N(6)	1817(10)	2196(11)	433(8)
C(7)	2882(14)	2285(15)	87(9)
O(7)	3658(9)	1326(10)	49(7)
O(8)	3059(10)	3574(10)	−208(8)
C(9)	2015(17)	4478(16)	−55(12)
C(10)	1157(14)	3565(13)	369(10)
Hg(2)	4025(1)	−1410(1)	581(1)
N(11)	3223(10)	−2091(12)	−465(7)
C(12)	2039(14)	−1825(15)	−715(9)
O(12)	1258(9)	−1154(10)	−397(7)
O(13)	1726(10)	−2345(13)	−1440(6)
C(14)	2814(18)	−3056(20)	−1704(11)
C(15)	3835(15)	−2912(17)	−1046(10)
N(16)	4839(11)	−817(13)	1627(7)
C(17)	4324(15)	68(16)	2096(9)
O(17)	3286(10)	658(11)	2026(7)
O(18)	5094(11)	320(12)	2763(7)
C(19)	6197(16)	−553(20)	2734(11)
C(20)	6102(14)	−1100(19)	1925(10)

shows that within the asymmetric unit there are two crystallographically independent HgL_2 units (Fig. 1). Each mercury atom is bound to two oxazolidone nitrogen atoms [Hg–N 2.002(12)–2.022(11) Å] in a nearly linear arrangement [N–Hg–N angles 176.6(5) and 177.7(4)°]. Each HgL_2 molecule is essentially planar and has its carbonyl groups in a *syn* orientation. Pairs of HgL_2 units are oriented face-to-face in an orthoganol relationship such that the carbonyl oxygens of one HgL_2 are linked to the mercury atom of the other, and *vice versa*, to form a dimer (Fig. 1) in which the non-bonded Hg(1) ··· Hg(2) distance is 3.56 Å.

Two oxygen atoms, one from each HgL_2 unit in the dimer, are binucleating and serve to link adjacent dimers so as to form a polymeric chain that extends in the crystallographic *a* direction (Fig. 2). Within these chains the Hg–O distances are in the range 2.733(9)–2.807(10) Å. The non-bridged Hg ··· Hg distances between adjacent oxygen-bridged dimers are both 4.01 Å and within the planar Hg_2O_2 bridging units the O–Hg–O angles are 87° and the transannular O ··· O distances are 3.8 Å.

Viewed down the *a* axis, the polymer chains are arranged in a near-hexagonal close-packed array (Fig. 3). This type of polymer-chain arrangement is closely reminiscent of that observed in the 1-methylhydantoin (1-methylimidazolidine-2,4-dione) mercury(II) complex,[10] though in that case the directions of the chain propagation alternate through the crystal, with adjacent chain axes being approximately orthogonal to each other. In the hydantoin compound the shortest Hg ··· Hg approach is 3.70 Å (*cf.* 3.56 Å in **1**).

Structures of the Compounds $Hg_2L_4M(NO_3)_3$.—Oscillation and Weissenberg photographs of single crystals of the complexes $Hg_2L_4Ln(NO_3)_3$, where M = La, Pr, Nd, Gd, Dy and Er, were taken to ascertain lattice parameters and these showed that they are all isostructural. Powder diffraction photographs demonstrated that this is also the case for $[Hg_2L_4Sm(NO_3)_3]$. Moreover although the analogous thulium and ytterbium compounds could not be obtained pure (they were contaminated with $[HgL_2]$) powder diffraction studies showed that these too are members of the same isostructural series. Previously[4] with the lactam–Hg–M complexes we have observed a distinct change in structure on going from Gd to Tb. Here, for the first time for this type of heterometallic complex, an identical structure is found across the lanthanide series from lanthanum through to ytterbium. Accordingly a full single-crystal X-ray analysis was carried out on a representative member of this series, $[Hg_2L_4Gd(NO_3)_3]$ **8**.

This shows that, as in compound **1**, each mercury atom is linked to the nitrogen atoms of two deprotonated oxazolidone

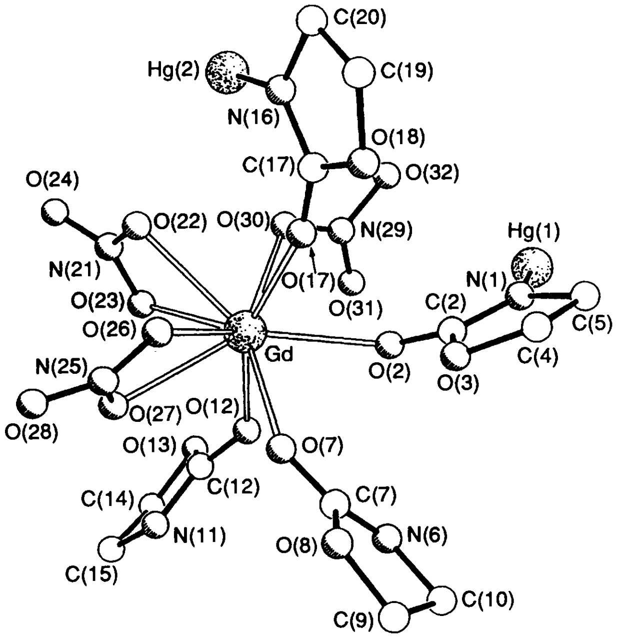


Fig. 4 The nine-co-ordinate arrangement about the gadolinium atom in complex **8**

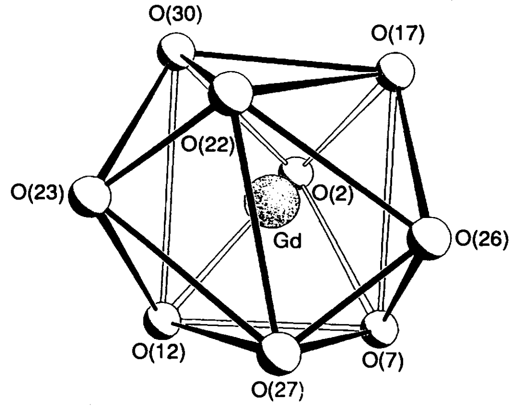


Fig. 5 The tricapped trigonal-prismatic co-ordination about the gadolinium atom in **8**

ligands in a near-linear arrangement [177.7(5)° at Hg(1) and 177.2(5)° at Hg(2)]; the Hg–N distances are in the range 2.007(12)–2.033(13) Å. The lanthanide atom has a co-ordination number of nine (Fig. 4), with a geometry best described as distorted tricapped trigonal prismatic (Fig. 5); O(2), O(23) and O(26) form the capping atoms. All the donor atoms are oxygen; four of them are carbonyl oxygen atoms from the ligand rings, four are from two bidentate nitrate groups and one is from a monodentate nitrate group. In the specific case of **8** the lanthanide–oxygen distances lie in two distinct groups, those to the carbonyl oxygens being in the range 2.32–2.41(1) Å and those to the nitrate oxygens being in the range 2.43–2.56(1) Å. The shortest of the latter group is that to the monodentate nitrate.

Adjacent gadolinium centres are linked *via* the L–Hg–L units to form a contiguous array of fused macrocycles (Fig. 6). In the metallamacrocyclic, polymeric, lactam–Hg–M complexes we have reported previously[1–6] there is a variety of ring sizes observed from one compound to another, but within each polymer there is a uniform ring size. Use of 2-oxazolidone introduces an unusual, new feature in that the polymeric array found for **8** contains fused rings of two different sizes. The linking of adjacent gadolinium centres *via* the L–Hg–L bridges generates an extended arrangement of contiguous 16- and 48-membered rings (Fig. 6). The closest comparison is with the 2-pyrrolidone **I** ($n = 2$) compounds. When four pyrrolidone

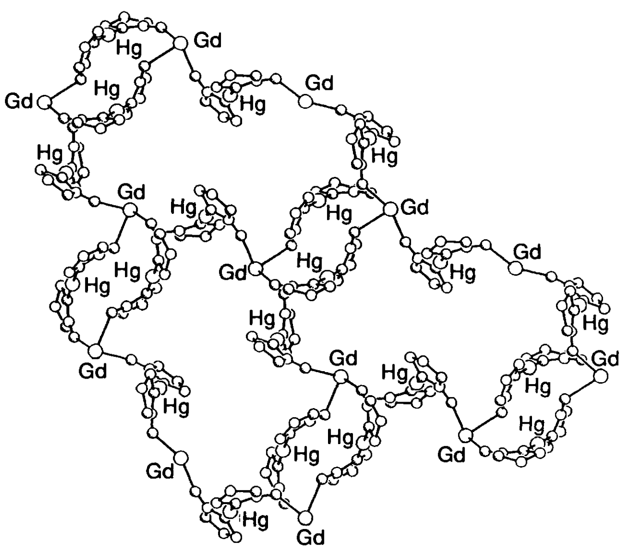


Fig. 6 Part of the contiguous array of 16- and 48-membered rings in the structure of complex **8** with the nitrate groups omitted for clarity

Table 3 Atomic coordinates (× 10^4) for complex **8**

Atom	*x*	*y*	*z*
Gd	659(1)	2021(1)	1303(1)
Hg(1)	1175(1)	−851(1)	1029(1)
N(1)	−386(12)	−350(7)	1500(8)
C(2)	−655(14)	332(7)	1324(10)
O(2)	7(10)	782(5)	936(7)
O(3)	−1808(9)	553(5)	1595(7)
C(4)	−2313(16)	−52(8)	2062(14)
C(5)	−1502(15)	−679(8)	1885(12)
N(6)	−2750(12)	1309(7)	−543(8)
C(7)	−2644(14)	1755(8)	173(10)
O(7)	−1646(10)	2065(5)	628(8)
O(8)	−3865(9)	1952(6)	400(8)
C(9)	−4873(17)	1640(11)	−297(14)
C(10)	−4157(15)	1077(10)	−804(13)
N(11)	200(12)	3040(6)	−1386(9)
C(12)	917(13)	2489(8)	−1003(10)
O(12)	652(10)	2050(5)	−389(7)
O(13)	2046(10)	2397(6)	−1391(7)
C(14)	1974(15)	2883(9)	−2213(11)
C(15)	860(19)	3417(10)	−2081(14)
N(16)	1600(12)	1476(7)	4320(8)
Hg(2)	3412(1)	1694(1)	3984(1)
C(17)	502(14)	1390(8)	3651(10)
O(17)	380(11)	1517(7)	2787(7)
O(18)	−526(11)	1138(7)	4041(8)
C(19)	−158(19)	1125(13)	5068(13)
C(20)	1328(18)	1236(11)	5272(11)
N(21)	3056(12)	2935(6)	1898(10)
O(22)	2290(10)	2732(5)	2489(7)
O(23)	2731(11)	2722(6)	1019(8)
O(24)	4039(12)	3307(7)	2162(8)
N(25)	−469(14)	3419(9)	1640(11)
O(26)	−518(12)	2931(7)	2249(8)
O(27)	59(11)	3316(6)	910(8)
O(28)	−915(17)	4050(9)	1776(11)
N(29)	2894(14)	727(10)	1430(16)
O(30)	2668(13)	1310(7)	1825(12)
O(31)	2744(18)	640(15)	600(14)
O(32)	3158(27)	236(10)	2058(17)
C(40)*	3040(49)	−264(27)	4297(42)
O(40)*	4001(41)	273(23)	4329(34)
C(40′)*	2955(58)	−161(34)	3740(52)
O(40′)*	4109(41)	258(24)	3887(33)

* Occupancy 0.5.

Table 4 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Hg(1)–N(1)	2.020(11)	Hg(1)–N(6)	2.022(11)
Hg(1)–O(12)	2.737(11)	Hg(1)····Hg(2)	3.562(1)
Hg(1)–O(17)	2.771(10)	Hg(1)–O(12′)	2.781(9)
O(2)–Hg(2)	2.807(10)	O(7)–Hg(2)	2.733(9)
O(7)–Hg(2″)	2.790(10)	N(11)–Hg(2)	2.022(11)
O(12)–Hg(1′)	2.781(9)	N(16)–Hg(2)	2.002(12)
Hg(2)–O(7″)	2.790(10)		
N(1)–Hg(1)–N(6)	176.6(5)	N(1)–Hg(1)–O(12)	90.7(4)
N(6)–Hg(1)–O(12)	92.4(4)	N(1)–Hg(1)–O(17)	92.4(4)
N(6)–Hg(1)–O(17)	87.2(4)	O(12)–Hg(1)–O(17)	122.1(3)
N(1)–Hg(1)–O(12′)	89.7(4)	N(6)–Hg(1)–O(12′)	89.0(4)
O(12)–Hg(1)–O(12′)	86.9(3)	O(17)–Hg(1)–O(12′)	150.8(3)
C(2)–O(2)–Hg(2)	135.5(9)	C(7)–O(7)–Hg(2)	138.0(10)
C(7)–O(7)–Hg(2″)	128.7(9)	Hg(2)–O(7)–Hg(2″)	93.1(3)
Hg(1)–O(12)–C(12)	136.8(9)	Hg(1)–O(12)–Hg(1′)	93.1(3)
C(12)–O(12)–Hg(1′)	129.8(10)	O(2)–Hg(2)–O(7)	120.9(3)
O(2)–Hg(2)–N(11)	87.3(4)	O(7)–Hg(2)–N(11)	87.8(4)
O(2)–Hg(2)–N(16)	91.9(4)	O(7)–Hg(2)–N(16)	94.5(4)
N(11)–Hg(2)–N(16)	177.7(4)	O(2)–Hg(2)–O(7″)	151.6(3)
O(7)–Hg(2)–O(7″)	86.9(3)	N(11)–Hg(2)–O(7″)	88.6(4)
N(16)–Hg(2)–O(7″)	91.2(4)	Hg(1)–O(17)–C(17)	133.0(10)

Atoms denoted (′) and (″) are related to their parent atoms by crystallographic symmetry.

Table 5 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **8**

Gd–O(2)	2.414(9)	Gd–O(7)	2.362(10)
Gd–O(12)	2.360(9)	Gd–O(17)	2.331(11)
Gd–O(22)	2.501(9)	Gd–O(23)	2.551(11)
Gd–O(26)	2.555(13)	Gd–O(27)	2.508(11)
Gd–O(30)	2.424(13)	Hg(1)–N(1)	2.033(13)
Hg(1)–N(6′)	2.020(12)	N(16)–Hg(2)	2.007(12)
Hg(2)–N(11″)	2.023(13)		
O(2)–Gd–O(7)	74.5(3)	O(2)–Gd–O(12)	81.7(3)
O(7)–Gd–O(12)	76.4(4)	O(2)–Gd–O(17)	74.9(4)
O(7)–Gd–O(17)	96.2(4)	O(12)–Gd–O(17)	156.5(4)
O(2)–Gd–O(22)	139.9(3)	O(7)–Gd–O(22)	137.8(3)
O(12)–Gd–O(22)	122.6(3)	O(17)–Gd–O(22)	77.8(4)
O(2)–Gd–O(23)	130.6(4)	O(7)–Gd–O(23)	134.5(3)
O(12)–Gd–O(23)	72.3(3)	O(17)–Gd–O(23)	124.6(3)
O(22)–Gd–O(23)	50.9(3)	O(2)–Gd–O(26)	126.9(4)
O(7)–Gd–O(26)	70.6(4)	O(12)–Gd–O(26)	125.4(4)
O(17)–Gd–O(26)	70.6(4)	O(22)–Gd–O(26)	67.9(3)
O(23)–Gd–O(26)	102.3(4)	O(2)–Gd–O(27)	144.3(3)
O(7)–Gd–O(27)	72.2(3)	O(12)–Gd–O(27)	78.5(3)
O(17)–Gd–O(27)	121.0(4)	O(22)–Gd–O(27)	75.5(3)
O(23)–Gd–O(27)	69.8(4)	O(26)–Gd–O(27)	50.7(4)
O(2)–Gd–O(30)	74.6(4)	O(7)–Gd–O(30)	149.0(4)
O(12)–Gd–O(30)	99.9(5)	O(17)–Gd–O(30)	74.8(5)
O(22)–Gd–O(30)	70.3(4)	O(23)–Gd–O(30)	69.8(4)
O(26)–Gd–O(30)	130.0(5)	O(27)–Gd–O(30)	137.9(4)
N(1)–Hg(1)–N(6′)	177.7(5)	Gd–O(2)–C(2)	133.4(9)
Gd–O(7)–C(7)	148.4(10)	Gd–O(12)–C(12)	137.8(9)
N(16)–Hg(2)–N(11″)	177.2(5)	Gd–O(17)–C(17)	162.2(10)
Gd–O(22)–N(21)	97.5(7)	Gd–O(23)–N(21)	95.2(8)
Gd–O(26)–N(25)	92.8(10)	Gd–O(27)–N(25)	95.1(9)
Gd–O(30)–N(29)	122.8(11)		

Atoms denoted (′) and (″) are related to their parent atoms by crystallographic symmetry.

anions bind to a lanthanide ion a chain polymer is formed, in which the basic repeat unit consists of only 16-membered $M_2Hg_2L_4$ rings. Here, the use of **II**, which has the same ligand ring size and utilises the same donor atoms as those of 2-pyrrolidone, produces a quite different overall structure. Two of the organic ligands bridge *via* the mercury atom to an adjacent centrosymmetrically related Gd forming a 16-membered ring. The other two, however, bridge *via* a glide-related gadolinium centre to another lattice-translated gadolinium creating a 48-membered centrosymmetric macrocycle. The latter ring contains 6 gadolinium, 6 mercury, 12 carbon 12 nitrogen and 12 oxygen atoms. The result is the coexistence of both 16- and 48-membered rings, each sharing a common edge (Fig. 6).

It is not immediately obvious why such an apparently small change in the nature of the organic ligand should result in such a dramatic change in the overall polymeric structure. However there is rotational flexibility about N–Hg–N in $[HgL_2]$; it is essentially planar in **1** but severely twisted in **8**, with the ligand rings inclined by *ca.* 120° to each other. Clearly, the degree of torsional twist will profoundly influence both the lanthanide–lanthanide separation and the directionality of propagation of the polymeric chains. The combination of these two variables must, to a large extent, influence the final, long-range structure adopted.

It is interesting that the ring oxygen of 2-oxazolidone is found not to be involved in any significant intra- or inter-molecular interactions. The included methanol solvent molecule is orientated such that both partial-occupancy oxygen atoms make a near-orthogonal approach (Hg–O *ca.* 2.7 Å) to one of the pairs of N–Hg–N units.

Vibrational Spectra.—Complexation of 2-oxazolidone results in the replacement of the strong ν(CO) IR band at 1740 cm^{-1} of the free ligand[11] by two strong bands, at 1704 and 1657 cm^{-1}, in the spectrum of **1**, two bands (1660 and 1618 cm^{-1}) in the spectra of the cobalt(II) (**14**) and zinc(II) (**15**) complexes, and three ν(CO) bands (*ca.* 1698, 1654 and 1620 cm^{-1}) for the lanthanide compounds.

The nitrate IR bands in the spectra of compounds **2**–**13** (see Experimental section) are as expected for the presence of both uni- and bi-dentate nitrate groups, but the spectrum of the cobalt complex **14** has bands consistent with ionic nitrate: 1384 (ν_3) and 831 cm^{-1} (ν_2).

Electronic Spectra.—The electronic spectrum of the cobalt(II) complex **14** is typical of an O_h CoO_6 chromophore, displaying relatively low-intensity bands at 7100 [ν_1,$^4T_{1g}(F) \longrightarrow {}^4T_{2g}$], 13 800 [$\nu_2$,$^4T_{1g}(F) \longrightarrow {}^4A_{2g}$] and 18 200 cm^{-1} [$\nu_3$,$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$]. The ν_2 band has its usual low intensity, and there is a shoulder at *ca.* 20 000 cm^{-1} due to contributions from spin-forbidden transitions.[12] This observation, taken in conjunction with the stoichiometry and the IR results, leaves little doubt that **14** is similar to the analogous complex with 2-pyrrolidone, in which each cobalt atom is octahedrally co-ordinated by six carbonyl oxygen atoms from the lactam ligands.[4a]

Three of the lanthanide complexes luminesce under visible–near-UV excitation. Under 397 nm excitation, the europium complex **7** shows phosphorescent emission with the dominant bands at 593 ($^5D_0 \longrightarrow {}^7F_1$) and 616.5 nm ($^5D_0 \longrightarrow {}^7F_2$) and with much weaker bands at 580 ($^5D_0 \longrightarrow {}^7F_0$), 645 ($^5D_0 \longrightarrow {}^7F_3$) and 693 nm ($^5D_0 \longrightarrow {}^7F_4$). The terbium complex **9** phosphoresces at 492 ($^5D_4 \longrightarrow {}^7F_6$), 546 ($^5D_4 \longrightarrow {}^7F_5$), 584 ($^5D_4 \longrightarrow {}^7F_4$) and 621 nm ($^5D_4 \longrightarrow {}^7F_3$), under 375 nm excitation. Under 351 nm excitation, the dysprosium complex **10** emits at 480 ($^4F_{\frac{9}{2}} \longrightarrow {}^6H_{\frac{15}{2}}$) and 574 nm ($^4F_{\frac{9}{2}} \longrightarrow {}^6H_{\frac{13}{2}}$).

The band energies of the solid-state electronic spectra of compounds **4**–**7** and **9**–**12** have been deposited as SUP 56931.

EPR Spectroscopy of Gadolinium(III)*-doped Compounds.*—The EPR spectra of Gd^{III}-doped samples of compounds **5**, **6**, **10** and **12** were measured at Q-band frequency. Analysis of the allowed transitions (SUP 56931), using the method set out previously[4b] gave for all four compounds a D value of $(245 \pm 5) \times 10^{-4}$ cm^{-1}, *i.e.* somewhat smaller than those found for the related 2-pyrrolidone complexes, and λ ($= E/D$) in the range 0.23–0.25, where D and λ are zero-field splitting

Table 6 Solid-state ^{13}C NMR data (δ)

2-Oxazolidone	1	2	6	Assignment
167.0	168.1	168.3	171.3	C=O
163.3	166.0	166.1	165.2	
66.0	67.6	71.4	69.7	C^5
		70.1		
		68.6		
42.0	48.6	49.3	49.6	C^4
	48.0			

parameters. These λ values are similar to those found for the 2-pyrrolidone complexes of stoichiometry $Hg_3M_2L_6(NO_3)_6$ formed by Eu, Tb and Y. The Q-band spectra each showed an additional weak, but well defined band at about 613 mT. This arises from a spin-forbidden ($DM_s = \pm 2$) transition of the gadolinium(III) ion.[4b]

Solid-state ^{13}C *NMR Spectra.*—As it is known[13] that the solid state (CP MAS) ^{13}C NMR spectra of some paramagnetic lanthanide compounds can show paramagnetic shifts analogous to those in solution, we have examined the solid-state NMR spectra of the compounds $[\{Hg_2L_4M(NO_3)_3\}_n]$ where M = La **2**, Pr **4** or Sm **6**. In order to minimise line-broadening effects, the praseodymium and samarium complexes were chosen as representative paramagnetic members of the series to compare with the results from the diamagnetic lanthanum complex.

In the diamagnetic lanthanum compound **2** the combined effect of Hg–N and La–O(carbonyl) bonding results in *ca.* 4–7 ppm shifts of all the ^{13}C resonances from their values for 2-oxazolidone itself (Table 6). The C^2 and C^5 resonances are split. Such splitting may arise from non-suppression by the MAS technique of the dipolar coupling between ^{14}N and ^{13}C of carbon atoms bonded to nitrogen[14] and/or from inequivalence of the 2-oxazolidone ligands in the crystal.

The spectrum of the samarium complex **6** is very similar to that of **2**; the bands are slightly broadened and the multiplet due to the carbonyl carbon shows only a small shift (samarium has the weakest paramagnetism of the paramagnetic lanthanides). Praseodymium(III) is considerably more paramagnetic and this was reflected in the spectrum obtained. The carbonyl peak was sufficiently broadened so as to disappear completely. The only resonance observed was a broad multiplet centred at δ *ca.* 55. The proton relaxation times, T_1, 2.51 (for **2**), 0.78 (**6**) and 0.21 s (**4**), respectively, show the expected trend and mirror the degree of broadening seen.

The ^{13}C NMR spectrum of the solid mercury complex $[HgL_2]$ was also measured (Table 6). This again showed small (2–6 ppm) shifts from the resonances observed for the free ligand. Its relaxation time (25.5 s) was far greater than those of the mixed-metal complexes.

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