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Synthesis and Characterization of some Metal Complexes with a New Nitrogen–Oxygen Donor Macrocyclic Ligand.
X-ray Structure of Diiodo(2,3:12,13-dibenzo-1,14,17-trioxa-5,10-diaza-2,3:4,5:10,11:12,13-cycloenneadecatetraene)Hg(II)

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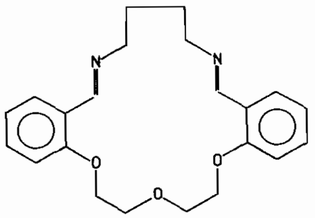
Crystals of $HgLI_2$ (L = (2,3:12,13-dibenzo-1,14,17-trioxa-5,10-diaza-2,3:4,5:10,11:12,13-cycloenneadecatetraene) prepared by adding the ligand in methanol-n-buthanol 1:1 mixture to a methanolic solution of HgI_2, are monoclinic ($P2_1/c$) with cell dimensions: a = *11.045(6),* b = *12.875(7),* c = *17.636(6) Å, β = 94.41(1)°, Z = 4. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to an* R *value of 5.34%. The metal is not included in the macrocycle ring: two nitrogens of two adjacent ligand molecules and two iodine atoms coordinate to Hg in a tetrahedral distorted arrangement. The structure consists also in polymeric chains running along the* b *axis.*

Introduction

As a part of a research program on the analytical and structural aspects of the chemistry of metal complexes with macrocyclic ligands [1–4], a new macrocycle with oxygen and nitrogen as donor atoms was synthesized. The aim of this study was to obtain a ligand with a large cavity, of suitable size to complex metals of relevant ionic radius.



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Complexes of this ligand with $AgNO_3$ and HgI_2 were obtained. The X-ray structural analysis of HgI_2, whose crystals were suitable, was undertaken to elucidate the conformation of the ligand in complexation and the steric properties of the complex.

Experimental

Preparation of the Ligand

0.1 mol of the sodium salt of the salicylaldehyde were dissolved by refluxing in DMF (250 cm^3); then bis-2,2-chloroethylether (0.05 mol) was added to this solution during 10 minutes. The reaction mixture was refluxed under nitrogen atmosphere for 20 h and then was poured into cold water and left to stand at 0 °C for two days. Pale yellow crystals precipitated with 50% yield.

0.1 mol of this compound were dissolved in hot absolute ethanol (50 cm^3) and 0.1 mol of 1,4-diaminobuthane were slowly added. The solution was refluxed for two hours, then poured into cold water and left to stand at 0 °C for some hours. The Schiff base precipitated as powder, which was recrystallized from ether; white needles were obtained (m.p. 114 °C, yield 95%).

The compound was characterized by elemental analysis, mass spectrum and IR spectroscopy.

Preparation of $HgLI_2$ and $AgLNO_3 \cdot H_2O$

10^{-3} mol of the ligand were dissolved in 50 cm^3 of hot methanol-n–buthanol 1:1 mixture. 10^{-3} mol of the appropriate inorganic salt in 50 cm^3 of methanol were added. The solution was heated for two hours under reflux. For both complexes white needle crystals precipitated by slow cooling. The compounds were characterized by elemental analysis, atomic absorption for metal, I.R. spectroscopy.

Mass Spectroscopy

The mass spectrum was run on a Varian MATCH5 at ionizing voltage of 20 eV. The solid sample was

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TABLE I. Crystal Data.

a = 11.045(6) Å β = 94.41(1)°
b = 12.875(7) $P2_1/c$
c = 17.636(6)
V = 2500(2) Å^3, M = 820.9, Z = 4, D_c = 2.18 g cm^{-3}
$F(000)$ = 1528, μ(MoKα) = 86.2 cm^{-1}

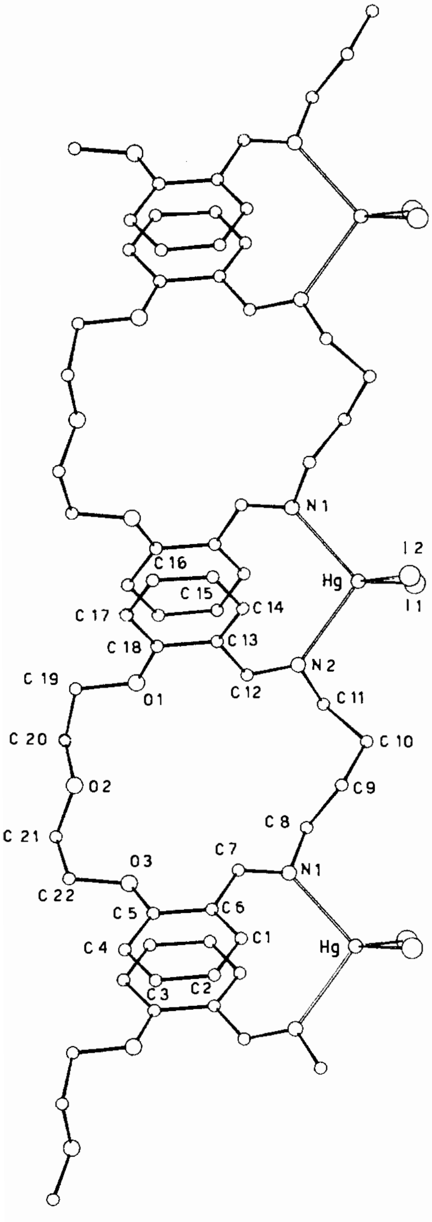

Fig. 1. Diagrammatic View of the Complex.

introduced into the source by direct insertion probe, the source temperature was 200 °C.

TABLE II. Fractional Atomic Coordinates (×10^4) with e.s.d.s in Parentheses.

	x	*y*	*z*
Hg	1384(1)	7179(1)	3814(1)
I(1)	153(1)	5384(1)	3733(1)
I(2)	268(2)	9043(1)	3841(1)
O(1)	6197(11)	7456(11)	2628(7)
O(2)	7524(14)	7527(12)	1283(8)
O(3)	6319(12)	8015(11)	–117(7)
N(1)	2845(12)	7771(13)	–122(7)
N(2)	2682(12)	7107(13)	2726(7)
C(1)	3875(17)	9563(15)	–976(10)
C(2)	4455(21)	10256(18)	–1449(12)
C(3)	5729(19)	10148(18)	–1466(11)
C(4)	6400(19)	9425(17)	–1023(10)
C(5)	5790(16)	8763(15)	–552(10)
C(6)	4516(16)	8812(15)	–550(9)
C(7)	3943(16)	8099(13)	–37(9)
C(8)	2469(16)	7065(16)	484(9)
C(9)	1711(16)	7690(16)	1041(9)
C(10)	1173(16)	6927(17)	1609(9)
C(11)	2124(17)	6365(15)	2160(10)
C(12)	3789(16)	7387(16)	2634(9)
C(13)	4452(18)	8131(15)	3119(10)
C(14)	3897(19)	8867(16)	3555(11)
C(15)	4556(21)	9587(19)	4010(12)
C(16)	5857(23)	9526(19)	4019(12)
C(17)	6425(18)	8839(19)	3569(12)
C(18)	5752(17)	8159(16)	3109(11)
C(19)	7519(16)	7418(19)	2600(12)
C(20)	7741(18)	6787(19)	1906(11)
C(21)	7919(18)	7122(21)	592(10)
C(22)	7626(16)	8016(18)	4(11)

IR Spectroscopy

IR spectra were run in the range 4000–250 cm^{-1} on a Perkin Elmer mod. 457 spectrophotometer with solid sample (KBr and PTFE were used as dispersing agents for $HgLI_2$ and $AgLNO_3 \cdot H_2O$ respectively).

Crystal Data and Intensities

Crystals of the title compound are monoclinic, space group $P2_1/c$. Preliminary crystal data were determined from rotation and Weissenberg photographs and successively were refined by least-squares using the 2θ values of 20 reflections ($\theta > 20°$) measured with a single crystal diffractometer. Intensity data were collected from a crystal 0.09 × 0.15 × 0.29 mm^3, on an on-line single-crystal automated Siemens AED diffractometer using niobium-filtered Mo-Kα radiation (λ = 0.7107 Å) and the ω–2θ scan technique (lowest speed 2.5° min^{-1}). In this way 5036 independent reflections ($0° < 2\theta < 52°$) were measured, 2760 of these, having $I > 2\sigma(I)$, were considered as observed and used in the analysis. Intensities were corrected for Lorentz and polarization factors and were converted to the absolute scale

TABLE III. Anisotropic Thermal Parameters ($\times 10^3$) with e.s.d.s in Parentheses.[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	40(1)	51(1)	37(1)	−4(1)	2(1)	1(1)
I(1)	45(1)	63(1)	69(1)	9(1)	9(1)	−12(1)
I(2)	54(1)	60(1)	101(1)	0(1)	−7(1)	16(1)
O(1)	31(6)	64(10)	45(7)	2(6)	−2(6)	−3(6)
O(2)	75(10)	77(12)	45(8)	−10(8)	12(7)	−20(9)
O(3)	40(7)	54(9)	48(8)	−1(7)	1(6)	−7(7)
N(1)	36(7)	48(9)	23(7)	−3(8)	5(6)	−2(8)
N(2)	32(7)	51(9)	24(7)	6(8)	1(6)	3(8)
C(1)	38(10)	43(11)	31(10)	−2(9)	0(8)	3(9)
C(2)	72(15)	55(14)	42(12)	−1(11)	−3(11)	26(12)
C(3)	45(12)	62(14)	43(12)	0(11)	8(10)	5(11)
C(4)	60(12)	56(13)	25(10)	8(9)	7(9)	17(11)
C(5)	42(11)	39(11)	24(9)	4(8)	2(8)	−13(9)
C(6)	38(10)	44(11)	19(8)	6(8)	7(7)	4(9)
C(7)	46(10)	39(11)	17(8)	10(7)	−2(7)	−4(8)
C(8)	49(10)	38(11)	28(9)	−16(9)	9(8)	4(10)
C(9)	39(9)	58(13)	26(9)	−5(9)	−2(7)	−5(9)
C(10)	35(10)	71(16)	26(9)	7(9)	9(8)	−3(10)
C(11)	44(11)	33(11)	31(10)	−8(9)	4(8)	−6(9)
C(12)	40(10)	55(13)	23(8)	13(8)	2(7)	−8(9)
C(13)	55(12)	41(12)	29(9)	12(8)	6(8)	−13(9)
C(14)	62(13)	47(12)	31(10)	5(9)	1(9)	−9(11)
C(15)	75(15)	61(15)	44(13)	−2(12)	31(11)	1(13)
C(16)	77(17)	62(15)	46(13)	8(12)	5(12)	−3(14)
C(17)	46(13)	73(16)	38(11)	8(11)	−4(10)	−22(11)
C(18)	34(10)	50(13)	35(12)	17(10)	6(9)	−3(9)
C(19)	27(10)	98(20)	52(12)	8(12)	0(9)	8(10)
C(20)	48(12)	84(16)	44(12)	22(11)	6(10)	15(11)
C(21)	44(11)	88(16)	42(11)	−3(13)	9(9)	−16(14)
C(22)	32(10)	83(17)	44(11)	1(11)	0(8)	−6(11)

[a] Anisotropic thermal parameters are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots 2hka^*b^*U_{12})]$.

TABLE IV. Principal Features of Mass Spectral Frequentation Patterns of the Ligand.

m/e	RI	Fragment
366	10	(M + H)
337	15	$(M-C_2H_5)$
297	100	$(M-[CH{=}N-(CH_2)_3]$
248	30	$CH_3(CH_2)_2O(CH_2)_2OC_6H_4CHN(CH_2)_4$

by Wilson's method. No correction for absorption was made.

Structure Determination and Refinement

A Patterson synthesis revealed the positions of the Hg and I atoms and a subsequent electron density map located all the non-hydrogen atoms. Refinement was carried out by full-matrix least-squares, first using isotropic thermal parameters, then anisotropic minimizing the function $\Sigma w|\Delta F|^2$ with unit weights. The final conventional R for all observed reflections was 5.34%. No attempts were made for localizing the hydrogen atoms. The atomic scattering factors used were taken from International Tables [5].

All the calculations were carried out on the CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale with the financial support of the University of Parma, using SHELX programs [6].

Crystal data are reported in Table I. The atomic fractional coordinates and thermal parameters are listed in Tables II and III. A list of the observed and calculated structure factors is available from the authors on request.

Results and Discussion

The IR spectrum of the ligand indicates the ring closure through the Schiff base condensation namely the ν(C=N) amine and aromatic stretching mode at 1640 and 1600 cm^{-1} are present. Mass spectral data (Table IV) agree with the cyclic structure.

TABLE V. Bond Distances (Å) and Angles (°) with e.s.d.s in Parentheses.^{a}

Hg–I(1)	2.680(2)	C(8)–C(9)	1.56(2)
Hg–I(2)	2.700(2)	C(9)–C(10)	1.55(3)
Hg–N(2)	2.48(1)	C(10)–C(11)	1.55(2)
Hg–N(1)^{i}	2.38(1)	C(12)–C(13)	1.44(3)
N(1)–C(7)	1.28(2)	O(1)–C(18)	1.36(2)
N(1)–C(8)	1.49(2)	O(1)–C(19)	1.47(2)
N(2)–C(11)	1.48(2)	O(2)–C(21)	1.42(2)
N(2)–C(12)	1.30(2)	O(3)–C(22)	1.44(2)
C(1)–C(2)	1.41(3)	C(13)–C(14)	1.39(3)
C(1)–C(6)	1.39(2)	C(13)–C(18)	1.44(3)
C(2)–C(3)	1.42(3)	C(14)–C(15)	1.39(3)
C(3)–C(4)	1.39(3)	C(15)–C(16)	1.44(3)
C(4)–C(5)	1.40(3)	C(16)–C(17)	1.37(3)
C(5)–C(6)	1.41(2)	C(17)–C(18)	1.37(3)
C(5)–O(3)	1.34(2)	C(19)–C(20)	1.50(3)
C(6)–C(7)	1.47(2)	C(21)–C(22)	1.57(3)
		O(2)–C(20)	1.46(3)
N(2)–Hg–N(1)^{i}	102.3(4)	N(1)–C(8)–C(9)	109(1)
I(2)–Hg–N(1)^{i}	104.2(4)	C(8)–C(9)–C(10)	109(1)
I(2)–Hg–N(2)	109.8(3)	C(9)–C(10)–C(11)	115(1)
I(1)–Hg–N(1)^{i}	112.1(4)	N(2)–C(11)–C(10)	110(1)
I(1)–Hg–N(2)	104.3(3)	N(2)–C(12)–C(13)	123(2)
I(1)–Hg–I(2)	122.5(1)	C(18)–O(1)–C(19)	117(1)
C(7)–N(1)–C(8)	116(1)	C(5)–O(3)–C(22)	118(1)
Hg–N(2)–C(12)	134(1)	C(12)–C(13)–C(18)	118(2)
Hg–N(2)–C(11)	108(1)	C(12)–C(13)–C(14)	124(2)
C(11)–N(2)–C(12)	116(1)	C(14)–C(13)–C(18)	118(2)
C(2)–C(1)–C(6)	122(2)	C(13)–C(14)–C(15)	123(2)
C(1)–C(2)–C(3)	117(2)	C(14)–C(15)–C(16)	117(2)
C(2)–C(3)–C(4)	123(2)	C(15)–C(16)–C(17)	122(2)
C(3)–C(4)–C(5)	119(2)	C(16)–C(17)–C(18)	120(2)
C(4)–C(5)–O(3)	125(2)	C(13)–C(18)–C(17)	120(2)
C(4)–C(5–C(6)	120(2)	O(1)–C(18)–C(17)	126(2)
C(6)–C(5)–O(3)	115(2)	O(1)–C(18)–C(13)	114(2)
C(1)–C(6)–C(5)	120(2)	O(1)–C(19)–C(20)	107(1)
C(5)–C(6)–C(7)	117(2)	C(20)–O(2)–C(21)	111(2)
C(1)–C(6)–C(7)	123(2)	O(2)–C(20)–C(19)	103(2)
N(1)–C(7)–C(6)	126(2)	O(2)–C(21)–C(22)	104(2)
		O(3)–C(22)–C(21)	105(1)

^{a}i = x, $3/2 - y$, $1/2 + z$.

The IR absorption of the two complexes are close to those of the free ligand. In the complexes the ν(C=N) mode is shifted to slightly lower frequencies (1630 cm^{-1}), indicating that the nitrogen atoms of the macrocycle are involved in the coordination. However the spectral data are not sufficient to define the conformation of the ligand and its behaviour in coordination.

Figure 1 shows the diagram of the structure. In Table V are quoted bond distances and angles. The results of the structural analysis of $HgLI_2$ complex, show that in this compound the metal is not included in the macrocycle ring. Two nitrogens of two adjacent ligand molecules and two iodide ions coordinate to Hg. All the structure can be also described as formed by polymeric chains running along the b axis.. Coordination around the metal is distorted tetrahedral; the angles mostly displaced from the theoretical tetrahedral value are I(1)HgI(2) = 122.5(1)° and N(2)HgN(1)^{i} (i = x, $3/2 - y$, $½ + z$) = 102.3(4)°. The dihedral angle between the planes defined by HgI(2)N(2) and HgI(1)N(1)^{i}, 86.4(1)° is indicative of the distortion of the tetrahedron. The Hg(II) environment is comparable to that found in the $Hg_3(en)_2I_6$ (en = ethylenediamine) [7], in which the Hg–I distances are 2.673(3) and 2.702(3) Å, the Hg–N 2.37(3) and 2.32(3) Å and the angles range from 78.9 to 121.3°. Hg–N distances greater than the sum of the tetrahedral covalent radii are found also in other Hg–N complexes [8].

Bond distances and angles in the macrocycle are in reasonable agreement with the values found in

TABLE VI. Torsion Angles (°) in the Macrocycle Ring.

C(6)C(7)N(1)C(8)	−179(2)
C(7)N(1)C(8)C(9)	101(2)
N(1)C(8)C(9)C(10)	172(1)
C(8)C(9)C(10)C(11)	65(2)
C(9)C(10)C(11)N(2)	71(2)
C(10)C(11)N(2)C(12)	−106(2)
C(11)N(2)C(12)C(13)	178(2)
N(2)C(12)C(13)C(18)	162(2)
C(12)C(13)C(18)O(1)	0(2)
C(13)C(18)O(1)C(19)	−178(1)
C(18)O(1)C(19)C(20)	−166(1)
O(1)C(19)C(20)O(2)	80(2)
C(19)C(20)O(2)C(21)	169(2)
C(20)O(2)C(21)C(22)	180(1)
O(2)C(21)C(22)O(3)	−71(2)
C(21)C(22)O(3)C(5)	175(1)
C(22)O(3)C(5)C(6)	−171(2)
O(3)C(5)C(6)C(7)	4(2)
C(5)C(6)C(7)N(1)	−155(2)

TABLE VIII. Contacts less than 3.6 A.

C(14)–N(1)^{i}	3.41(2)
N(2)–C(1)^{i}	3.34(2)
C(12)–C(1)^{i}	3.51(3)
O(1)–C(4)^{i}	3.39(2)
C(18)–C(5)^{i}	3.42(3)
C(12)–C(6)^{i}	3.59(2)
C(13)–C(6)^{i}	3.43(2)
C(14)–C(7)^{i}	3.54(3)
C(17)–O(3)^{i}	3.34(3)
C(18)–O(3)^{i}	3.49(2)

i = *x*, 3/2 − *y*, 1/2 + *z*

other macrocyclic ligands [1–3, 9]. The present bond distances may suffer to some extent from greater inaccuracies due to the presences of the heavy mercury and iodine atoms, which dominate the X-ray scattering. In Table VI main torsion angles in the macrocycle ring are quoted. The conformation of the macrocycle in the O–C–C–O–C–C–O chain is *anti–gauche–anti–anti–gauche–anti* and in N–C–C–C–C–N *eclipsed–anti–gauche–gauche–eclipsed.* It is noteworthy that in the later chain coordination to metal is responsible of the exo conformation of the nitrogen atoms which probably are endo in the free ligand as the oxygen atoms. In Table VII, the analyses of the most significant planes are reported, the greatest displacement from the mean plane through the five possible donor atoms involves O(2) (0.2 Å).

TABLE VII. Analyses of the Most Significant Planes with Displacements of Each Atom.

PLANE C(1)C(2)C(3)C(4)C(5)C(6)	−0.06002*X* − 0.65689*Y* − 0.75246*Z* = −7.03890[a]
C(1) −0.01(2), C(2) −0.01(2), C(3) 0.02(2), C(4) 0.00(2), C(5) −0.02(2), C(6) 0.02(2) A	
PLANE C(13)C(14)C(L5)C(15)C(16)C(17)C(18)	0.01115*X* + 0.65581*Y* − 0.75485*Z* = 2.8152
C(13) −0.02(2), C(14) −0.01(2), C(15) 0.02(2), C(16) −0.03(2), C(17) 0.00(2), C(18) 0.03(2) A	
PLANE O(1)O(2)O(3)N(1)N(2)	0.05149*X* − 0.98701*Y* − 0.15203*Z* = −9.69582
O(1) −0.14(1), O(2) 0.21(1), O(3) −0.09(1), N(1) 0.02(2), N(2) 0.07(2) A	
PLANE C(13)C(14)C(15)C(16)C(17)C(18)C(12)N(2)C(11)O(1)C(19)C(20)	−0.08241*X* + 0.65524*Y* − 0.75091*Z* = 2.31988
C(13) 0.05(2), C(14) 0.15(2), C(15) 0.10(2), C(16) −0.08(2), C(17) −0.12(2), C(18) −0.03(2), C(12) 0.12(2), N(2) −0.14(1), C(11) 0.03(2), O(1) −0.03(1), C(19) −0.15(2), C(20) 0.20(2) A	
PLANE C(1)C(2)C(3)C(4)C(5)C(6)C(7)C(8)N(1)O(3)C(22)C(21)	0.02482*X* − 0.64882*Y* − 0.76054*Z* = −6.43712
C(1) −0.13(2), C(2) −0.06(2), C(3) 0.08(2), C(4) 0.11(2), C(5) 0.02(2), C(6) −0.06(2), C(7) −0.17(2) C(8) −0.04(2), N(1) 0.19(1), O(3) 0.07(1), C(22) −0.05(2), C(21) −0.09(2) A	

[a] *X*, *Y*, *Z* are the orthogonal coordinated obtained from the fractional ones applying the matrix ‖ *a* 0 *c*cosβ | 0 *b* 0 | 0 0 *c*sinβ ‖.

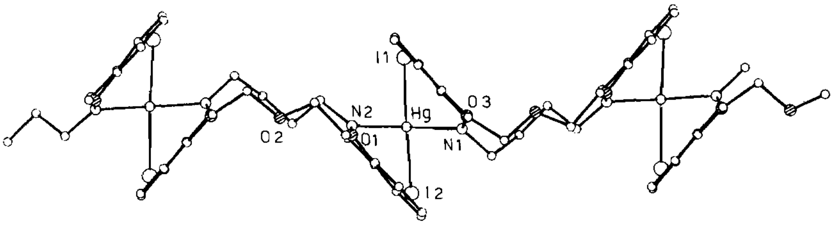

Fig. 2. Projection along [100].

It can be noticed that some pseudosymmetries between adjacent macrocycle molecules are present in the structure, as these molecules can be considered related by a twofold non-crystallographic axis through the $N(1)^{i}HgN(2)$ bisector. Also in the macrocyle two nearly symmetric parts related by a non-crystallographic plane through O(2) and the middle point of the O(8)–C(11) line can be visualized if the C(9)–C(10) group is excluded. The two parts of the ligand are roughly planar and nearly perpendicular, the dihedral angle between their mean planes being $81.7(2)^\circ$ (Fig. 2). The two benzene rings are nearly parallels (dihedral angle $4.1(1)^\circ$) and show C···C distances in the range 3.41–3.44 Å. Packing is determined by the C···C interactions and by van der Waals contacts quoted in Table VIII.

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