



Stereochemically non-rigid helical mercury(II) complexes

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ARTICLE INFO

Article history:

Received 9 October 2008

Accepted 7 November 2008

Available online 18 November 2008

Keywords:

Mercury

Helical

Spiral

N ligands

Crystal structures

ABSTRACT

Reactions of the 1:2 condensate (L) of benzil dihydrazone and 2-acetylpyridine with $\text{Hg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ and HgI_2 yield yellow $[\text{HgL}_2](\text{ClO}_4)_2$ (**1**) and HgLI_2 (**2**), respectively. Homoleptic **1** is a 8-coordinate double helical complex with a $\text{Hg}(\text{II})\text{N}_8$ core crystallising in the space group $Pbca$ with cell dimensions: $a = 16.2250(3)$, $b = 20.9563(7)$, $c = 31.9886(11)$ Å. Complex **2** is a 4-coordinate single helical complex having a $\text{Hg}(\text{II})\text{N}_2\text{I}_2$ core crystallising in the space group $P2_1/n$ with cell dimensions $a = 9.8011(3)$, $b = 17.6736(6)$, $c = 16.7123(6)$ Å and $\beta = 95.760(3)^\circ$. In complex **1**, the N-donor ligand L uses all of its binding sites to act as tetradentate. On the other hand, it acts as a bidentate N-donor ligand in **2** giving rise to a dangling part. From variable temperature ^1H NMR studies both the complexes are found to be stereochemically non-rigid in solution. In the case of **2**, the solution process involves wrapping up of the dangling part of L around the metal.

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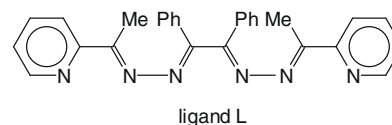
1. Introduction

A helical structure for a metallo organic complex was first proposed by Harries and McKenzie in 1969 in regard of a dinuclear copper(II) complex of bis(pyridinal)ethylenediamine [1]. It has gone largely unnoticed. The first crystal structure of a helical metal complex is possibly that of a Co(II) compound reported by Wester and Palenik in 1975 [2]. Systematic studies on helical complexes actually have started in the mid-eighties with the pioneering works of Lehn [3,4]. Examples of helical metallo organic compounds are now numerous. In all these cases the organic component (ligand) containing suitable donor atoms is non-helical. But the coordination properties of the metal ions direct the wrapping of the ligand around them in such a manner that an overall helical topology is assumed.

For quite some time we have been interested in helical complexes [5–12]. A dinuclear Cu(I) helicate of ours [6] has subsequently been optically resolved by Wild and co-workers [13]. We have been working mainly with ligands which themselves are helical. Thereby we have been able to produce mononuclear double helical complexes; in some cases the metal ion is square planar. Lehn's approach does not provide for mononuclear helical complexes, the possibility of which was not then considered. Herein we report two novel mononuclear helical complexes of mercury(II) generated by using a helical N-donor ligand.

2. Results and discussion

Our ligand L here is derived from benzil dihydrazone which has a helical twist [14]. It is a 1:2 condensate of benzil dihydrazone and 2-acetylpyridine [15,16]. The $\text{N}=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{N}$ torsion angle which in benzil dihydrazone is $\sim 70^\circ$ becomes $85.9(5)^\circ$ in L. Thus L itself is helical.



Reaction of L with $\text{Hg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ in 2:1 molar proportion in methanol at room temperature yields $[\text{HgL}_2](\text{ClO}_4)_2$ (**1**). While L is reacted with HgI_2 in equimolar proportion in dimethylformamide-methanol mixture at room temperature, we obtain HgLI_2 (**2**).

The crystal structure of **1** consists of a discrete $[\text{HgL}_2]^{2+}$ cation (Fig. 1) together with two ClO_4^- anions. In the cation, the mercury atom is bonded to two ligands both acting as tetradentate. There is a wide range of Hg–N distances indicating that the structure is particularly strained. It is noteworthy that the Hg–N dimensions in one ligand N(11), N(18), N(23), N(30) at 2.48(1), 2.62(1), 2.78(1), 2.59(1) Å, respectively, are longer than their counterparts in the other ligand N(41), N(48), N(53), N(60) at 2.35(1), 2.53(1), 2.57(1), 2.37(1) Å. The torsion angles for each ligand are given in Table 1.

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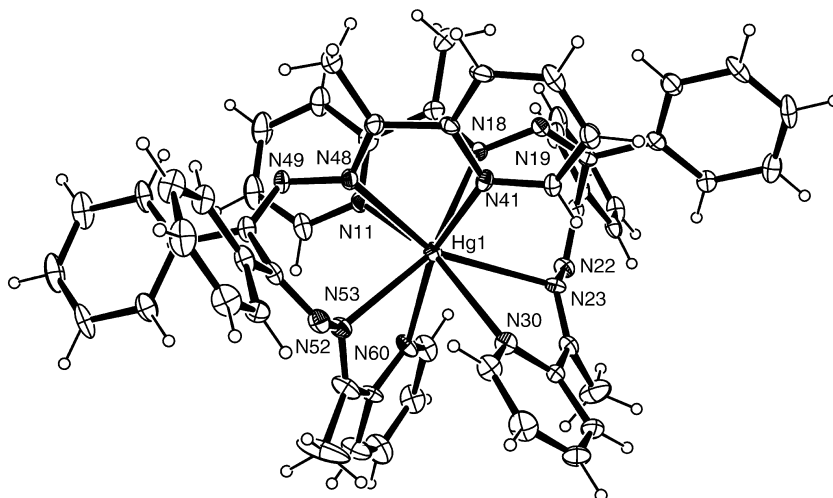


Fig. 1. The structure of the cation in **1** with ellipsoids at 25% probability. For Hg–N distances, see text. Selected bond angles ($^{\circ}$): N41–Hg1–N60 160.8(3), N41–Hg1–N11 118.2(3), N60–Hg1–N11 80.9(3), N41–Hg1–N48 65.7(2), N60–Hg1–N48 126.3(3), N11–Hg1–N48 74.0(2), N41–Hg1–N53 111.1(2), N60–Hg1–N53 66.2(2), N11–Hg1–N53 95.5(3), N48–Hg1–N53 70.0(3), N41–Hg1–N30 81.6(2), N60–Hg1–N30 79.3(3), N11–Hg1–N30 160.1(2), N48–Hg1–N30 120.0(2), N53–Hg1–N30 78.0(3), N41–Hg1–N18 74.1(2), N60–Hg1–N18 116.7(2), N11–Hg1–N18 63.0(2).

Table 1
Some torsion angles in the ligand backbones in **1** and **2**.

	1		2
	Ligand 1	Ligand 2	
N(11)–C(16)–C(17)–N(18)	–7.7(1)	–11.1(1)	–11.0
C(16)–C(17)–N(18)–C(19)	175.1(7)	177.7(7)	78.2(5)
C(17)–N(18)–N(19)–C(20)	137.3(8)	123.6(9)	137.1(6)
N(18)–N(19)–C(20)–C(21)	8.3(1)	8.4(1)	–3.4(8)
N(19)–C(20)–C(21)–N(22)	84.9(1)	74.8(1)	100.0(8)
C(20)–C(21)–N(22)–N(23)	–6.1(1)	0.2(1)	–2.1(8)
C(21)–N(22)–N(23)–C(24)	154.1(8)	137.2(1)	161.5(6)
N(22)–N(23)–C(24)–C(25)	175.6(7)	176.7(8)	–173.7(5)
N(23)–C(24)–C(25)–N(30)	–27.1(1)	–24.3(1)	–178.8(6)

The crystal structure of **2** is shown in Fig. 2 together with the atomic numbering scheme. Here the metal has a 4-coordinate tetrahedral environment being bonded to two iodine atoms at 2.65(0), 2.65(0) Å and two nitrogen atoms of the ligand L, N(11) at 2.40(1) and N(18) at 2.50(1) Å. The other potential donor nitro-

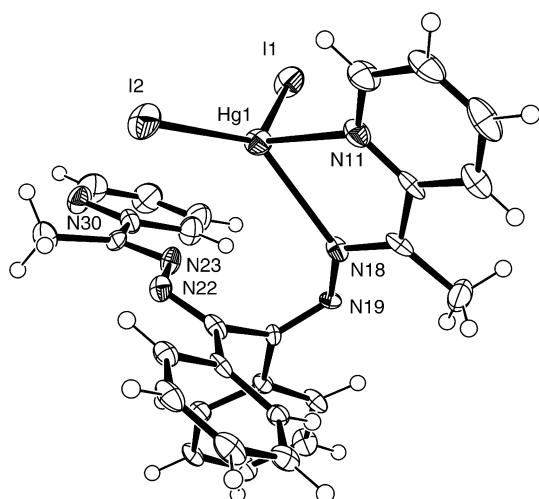


Fig. 2. The structure of **2** with ellipsoids at 50% probability. Selected bond distances (Å) and angles ($^{\circ}$): Hg1–N11 2.40(1), Hg1–N18 2.50(1), Hg1–I1 2.65(0), Hg1–I2 2.65(0), N11–Hg1–N18 66.6(2), N11–Hg1–I1 112.6(2), N18–Hg1–I1 104.0(1), N11–Hg1–I2 97.7(1), N18–Hg1–I2 123.5(1), I1–Hg1–I2 131.05(2).

gen atoms are unbonded with Hg...N distances >3.23 Å. The distortions from tetrahedral geometry are primarily introduced by the small bite angle of the ligand, N(11)–Hg(1)–N(18) being $66.6(2)^{\circ}$ which is concomitant with an extended I(1)–Hg(1)–I(2) angle of $131.05(2)^{\circ}$. The torsion angles in the ligand are given in Table 1 and show very little difference from those observed in the ligands acting as tetradentate donor atoms in **2**. Clearly just a small increase in the N(19)–C(20)–C(21)–N(22) torsion angle is sufficient to remove N(22) from the coordination sphere; this torsion angle [$100.0(8)^{\circ}$] is greater than that in the free ligand. It is also noteworthy that at the non-chelating part of the ligand, the N(23)–C(24)–C(25)–N(30) is *trans* rather than *cis* as is found in **2**. Such *trans* configuration is found in the free ligand.

The morphologies of both the complexes **1** and **2** are helical. While single helical nature of complex **2** is quite apparent from Fig. 2, the double helical nature of **1** can be discerned better in Fig. 3. These complexes are stereochemically non-rigid in solution as revealed by variable temperature ^1H NMR studies.

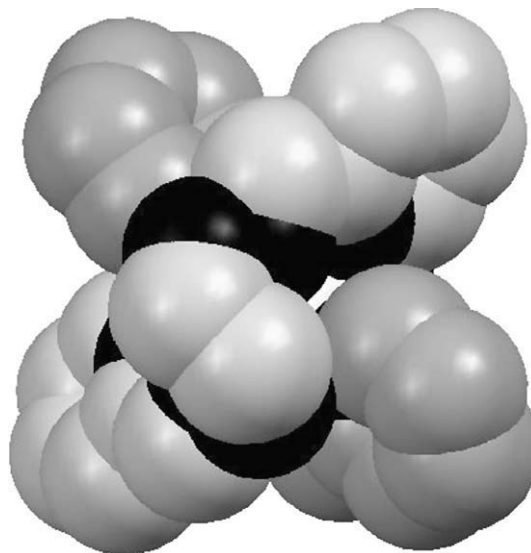


Fig. 3. A space filling model of the cation in **1** showing its helical nature of the complex. The methyl and phenyl groups, and H atoms are removed for clarity. Colour code: N, black; Hg, white; C in one of the ligand strands is dark grey and in the other light grey.

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