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Coordination geometry isomerism induced by N–H···Cl, C–H···Cl, C–H···N, C–H···π and π···π supramolecular interactions in mercury(II) complexes with tripyridylimidazole chelating ligands

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Abstract

Reaction of $HgCl_2$ with *trans*-(±)2-(2,5-di(pyridin-2-yl)-4,5-dihydro-1*H*-imidazol-4-yl)pyridine (**L1**) and *cis*-(±)-(phenyl(2,4,5-tri(pyridin-2-yl)-4,5-dihydroimidazol-1- yl)methanone (**L2**) gives mononuclear complexes, **1** and **2**. In these complexes **L1** and **L2** behave as tridentate and bidentate chelating ligands, giving distorted trigonal bipyramidal and tetrahedral coordination geometries, respectively. X-ray diffraction studies revealed a series of N–H···Cl, C–H···Cl, C–H···N and C–H···π interactions in **1** giving a 3D network, and N–H···Cl, C–H···Cl, C–H···π and π···π interactions in **2** giving a 2D network in the crystal lattice. Since both ligands should have a similar binding capacity to the mercury ions, the variations observed for coordination number and geometry should be a consequence of supramolecular stabilizing effects.

Keywords: Imidazole ligands; Mercury complexes; Noncovalent interactions; X-ray structures; Supramolecular networks

1. Introduction

The crystal engineering of supramolecular architectures or metal–organic coordination polymers is a growing field that has attracted much attention in the past decades [1–4]. Inorganic–organic hybrid materials have been studied for potential application in gas storage, catalysis, separations, and molecular recognition [5]. Organic components containing N- or O-donors in the framework offer a great potential for chemical and structural diversity [6]. With the recent development of self-assembly strategies, it is possible to rationally design and synthesize supramolecular architectures or metal–organic coordination polymers based on covalent or supramolecular contacts and dispersion forces [7]. Among weak noncovalent forces, hydrogen bonds are commonly used as structure directing entities and hence allow their application on crystal design. The relevance of C–H···π interactions in coordination and organometallic chemistry has been shown by a number of research groups [8–10]. They can influence the conformation of molecules, self-assembly processes as well as induce chiral recognition [11]. In contrast, to date little attention has been paid by inorganic chemists to the effect that N–H···Cl, C–H···Cl, and π···π interactions can have on the solid-state coordination geometry of metal complexes [12].

Mercury(II) complexes have been the focus of many recent studies [13]. In these complexes the metal ions exhibit a range of different coordination geometries such as linear [14], trigonal-planar [15], square-planar [16], tetrahedral [17], trigonal-bipyramidal [18], square-pyramidal [19] and octahedral [20], depending on the ligand geometry and reaction conditions.

In the course of our ongoing studies on the coordination behavior of polypyridyl ligands, recently, we became

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interested in analyzing the influence that primarily weak hydrogen bonding interactions can have on the supramolecular structure of metal complexes [21]. Neutral $LHgCl_2$ complexes containing the aromatic chelating ligands *trans*-(±)2-(2,5-di(pyridin-2-yl)-4,5-dihydro-1*H*-imidazol-4-yl)pyridine (**L1**) [22] and *cis*-(±)-phenyl[2,4,5-tri(pyridin-2-yl)-4,5-dihydroimidazol-1-yl]methanone (**L2**) [23] are ideal candidates for this purpose, since in these cases X–H···Cl (X = C, N), C–H···N, C–H···π and π···π interactions are possible. Interestingly, we found that the contribution these interactions have to the crystal lattice energy can induce a change of the coordination number and geometry of the mercury atom.

2. Experimental

2.1. General remarks

All chemicals were used as received without further purification. The synthesis and spectroscopic data for **L1** [22] and **L2** [23] have been reported elsewhere. Infrared spectra (KBr) were measured on a Perkin–Elmer 1600 series instrument. NMR spectra were recorded at 200 MHz with a Varian Mercury spectrometer at 25 °C using DMSO-d_6 as the solvent and TMS as reference. FAB mass spectra were obtained using a JMS-700 MSTATION. Elemental analyses were performed on a Vario EL equipment.

2.2. Complexes

2.2.1. [Hg(L1)(Cl)$_2$] (1)

$HgCl_2$ (0.07 g, 0.257 mmol) was added as a solid to a solution of **L1** (0.084 g, 0.257 mmol) in dichloromethane (5 mL). After 3 h of stirring at room temperature a white solid precipitated. The product was collected by filtration and dried under vacuum. Recrystallization of the precipitate from DMF/Et_2O gave **1** as colorless single crystals. Yield (0.132 g, 0.230 mmol, 89%) IR (KBr): 3242, 3052, 2861, 1614, 1580, 1562, 1533, 1465, 1433, 1219, 1000, 784, 748 cm^{-1}. ^1H NMR (DMSO-d_6, 200 MHz): δ 8.60–8.50 (m, 3H), 8.25–8.12 (m, 2H), 7.92–7.82 (m, 3H), 7.56 (d, $J = 7.8$ Hz, 2H), 7.40–7.34 (m, 2H), 5.49 (s, 2H). MS [FAB^+, *m*/*z* (%)]: 538 (5) $[M-Cl]^+$, 460 (8) $[M-Py-Cl]^+$ 302 (100) $[(M+H)-HgCl_2]^+$. HR-FAB^+ calc. for $[M-Cl]^+$, $C_{18}H_{15}ClHgN_5$: 538.0732. Found: 538.0751 (+5.3 ppm). *Anal.* Calc. (%) for $C_{18}H_{15}N_5HgCl_2$: C: 37.74, H: 2.64, N: 12.22. Found: C: 37.78, H: 2.66, N: 12.07.

2.2.2. [Hg(L2)(Cl)$_2$] (2)

The complex was synthesized in the same way as compound **1**, replacing **L1** by **L2** to obtain a colorless crystalline solid. Yield (0.070 g, 0.184 mmol, 63%). IR (KBr): 3052, 2995, 2861, 1676, 1595, 1566, 1461, 1438, 1385, 1333, 1156, 924, 745, 716 cm^{-1}. ^1H NMR (DMSO-d_6, 200 MHz): δ 8.33 (t, $J = 5.6$ Hz, 2H), 8.17 (dd, $J = 4.0$, 0.6 Hz 1H), 7.86–7.76 (m, 2H), 7.56–7.45 (m, 2H), 7.40–7.24 (m, 4H) 7.18–6.99 (m, 6H), 6.17 (d, $J = 9.4$ Hz, 1H), 6.10 (d, $J = 9.4$ Hz, 1H). MS [FAB^+, *m*/*z* (%)]: 642 (3) $[M-Cl]^+$, 424 (4) $[M-(C_6H_5O)-Py-Cl]^+$, 406 (62) $[(M+H)-HgCl_2]^+$. HR-FAB^+ calc. for $[M-Cl]^+$, $C_{25}H_{19}ClHgN_5O$: 642.0984. Found: 642.0925 (−9.2 ppm).

2.2.3. X-ray crystallography

X-ray quality crystals were grown by vapor phase diffusion of diethyl ether into a concentrated solution of the complexes in dmf. A summary of the crystallographic data and refinement parameters for the structural analyses is given in Table 1. X-ray diffraction studies were performed on a Bruker-AXS diffractometer with a CCD area detector ($\lambda_{MoK\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at $T = 293$ K via ω/Φ-rotation at 10 s per frame (SMART) [24]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [25]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [26]. Non hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions using a riding model. N–H hydrogen atoms have been localized by difference Fourier maps, but their D–H distances and U_{iso} factors have been fixed (0.86 Å for N–H and $U_{iso} = 1.5$ times the U_{equiv} value of the neighboring donor atom).

Table 1
Crystallographic data and collection parameters for **1** and **2**

	1	**2**
Empirical formula	$C_{18}H_{15}HgN_5Cl_2$	$C_{25}H_{19}HgN_5OCl_2$
MW (g mol^{-1})	572.84	676.94
Space group	$P\bar{1}$	*Pbca*
a (Å)	9.4847(10)	15.9289(13)
b (Å)	9.7142(10)	11.5138(9)
c (Å)	11.2281(16)	26.476(2)
α (°)	115.377(2)	90
β (°)	95.416(3)	90
γ (°)	94.778(2)	90
V (Å^3)	921.67(19)	4855.7(7)
Z	2	8
ρ_{calc} (g cm^{-3})	2.064	1.852
μ (mm^{-1})	8.652	6.588
θ limits (°)	$2.03 < \theta < 25$	$1.54 < \theta < 25$
Number of collected reflections	4787	44250
Number of indepependent reflections (R_{int})	3116 (0.024)	4271 (0.091)
Number of observed reflections[a]	2784	3439
R[b]	0.038	0.067
R_w[c]	0.044	0.086
Goodness-of-fit	0.989	1.266
$\Delta\rho_{max}$ (e Å^{-3})	1.640	1.062

[a] $I > 2\sigma(I)$.
[b] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$.
[c] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.