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Preparation of mercury–anthracene derivatives: π–π-stacking, Hg···Cl and Hg···π interactions in the X-ray crystal structure of polymeric 9-chloromercurioanthracene[☆]

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Abstract

9-Lithio-anthracene and 9,10-dilithioanthracene react with mercury(II)chloride in THF to afford 9-chloromercurio-anthracene (**1**) and 9,10-bis(chloromercurio)-anthracene (**2**), respectively. Compounds **1** and **2** have been characterized by ^{1}H-, ^{13}C- and ^{199}Hg-NMR spectroscopy as well as by elemental analysis and CI mass spectrometry. The structure of **1** has been determined by X-ray crystallography. In the solid state, **1** forms polymeric chains that are cemented by concomitant π–π-stacking, Hg···Cl and Hg···π-system interactions. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Organomercurials rarely form isolable adducts with neutral or anionic nucleophiles [1,2]. However, in the solid state, the mercury center of these compounds often engages in secondary weak interactions with vicinal electron-rich moieties. Thus, inter- and intra-molecular Hg···O, Hg···N, Hg···S and Hg···X (X = halide) interactions are common occurrences in the solid state structures of organomercurials containing these heteroatoms [3]. In the case of organomercuryhalides, these interactions usually lead to the formation of oligomers or even polymers with ladder-type structures in which the monomeric units are connected by head to tail Hg_2X_2 bridges [4]. This aggregation pattern is highly predictable and can be used in the design of supramolecular assemblies [5]. Following some of our recent work on the supramolecular structure of organomercuryhalides [5,6], it became our aim to prepare solids in which the molecular components are assembled through different types of associative interactions. Because of the current interest in understanding and rationalizing π–π-stacking interactions [7], it was decided to engineer crystals in which both Hg···X and π–π-stacking interactions occur concomitantly. It occurred to us that such a goal could be attained by preparing organomercuryhalides bearing large aromatic ligands such as anthracene [8].

2. Results and discussion

2.1. Synthesis

The monomercurated derivative 9-chloromercurio-anthracene (**1**) can be prepared by reaction of 9-lithio-anthracene with mercury(II)chloride. Compound **1** is a bright yellow air-stable solid. Although it is insoluble in organic solvents of low polarity, it readily dissolves in

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[☆] Dedicated to Alan H. Cowley on the occasion of his 65th birthday.

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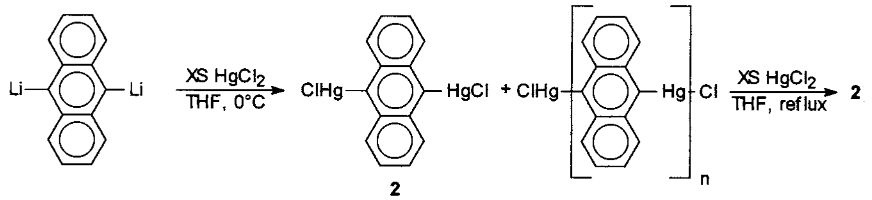

Scheme 1.

DMF and DMSO. The ^{1}H- and ^{13}C-NMR spectrum of **1** exhibits the expected resonances for a 9-substituted-anthracene derivative. In the ^{199}Hg-NMR spectrum, one signal is detected at −1100 ppm, confirming the presence of a mercury atom in the complex. Additional characterization of compound **1** was provided by CI mass spectrometry, which allowed the detection of the molecular peak. In the solid state, compound **1** fluoresces at $\lambda_{\text{emission}} = 465$ nm when irradiated at $\lambda_{\text{excitation}} = 355$ nm.

9,10-Bis(chloromercurio)-anthracene (**2**) can be prepared by an analogous procedure. Hence, 9,10-dilithioanthracene reacts with mercury(II)chloride in THF to afford, after reflux, a bright yellow solid. If the reaction mixture is not brought to reflux for several hours, a yellow solid is still isolated. However, elemental analysis indicates that the composition of this latter solid differs from that of **2**, and apparently corresponds to a mixture of **2** and oligomeric complexes in which several 9,10-anthracenediyl ligands are linked by mercury centers (Scheme 1). These putative oligomeric complexes can be regarded as an intermediate product since the solid material reacts with additional mercury(II)chloride in THF under reflux to afford pure **2** (Scheme 1). Like other bifunctional organo-mercury-halides [5,6], such as 1,8-bis(chloromercurio)-naphthalene [9] or 1,2-bis(chloromercurio)-benzene [10], compound **2** is insoluble in most organic solvents except DMSO, in which it is sparingly soluble. This low solubility complicated the collection of satisfactory NMR data. While the expected proton signals were readily detected in a high temperature measurement (100°C, DMSO-d_6), no ^{199}Hg-NMR signal could be obtained under the same conditions despite prolonged acquisition time. Unambiguous identification of **2** was provided by elemental analysis and CI mass spectrometry.

2.2. Structure of 9-chloromercurio-anthracene

The growth of diffraction-quality crystals of **2** was hampered by its low solubility, which invariably led to the rapid precipitation of polycrystalline materials. In contrast, crystals of **1** were grown conveniently by slow evaporation of a DMF solution. Fig. 1 shows an ORTEP diagram of a molecule of **1**. It is noteworthy that the mercury and chlorine atoms are displaced by 0.28 and 0.74 Å above the plane containing the anthracenyl ligand, thus conferring an approximate C_s symmetry to the molecule. This deviation is most certainly a consequence of the aggregation mode adopted by **1** in the solid state (Fig. 2). Examination of the cell-packing diagram indicates that **1** forms discrete polymeric chains. The anthracenyl ligands are strictly parallel to one another and generate π-stacks. Rather than being rigorously superimposed the anthracenyl ligands are slipped with respect to one another. As a result of this slippage, the carbon atoms C(5b), C(12b), C(10b), C(13b), C(4b) and C(3b) are respectively positioned on top of C(7a), C(8a), C(11a), C(9a), C(14a) and C(1a) in a direction almost orthogonal to the anthracenyl plane. The distances between the carbon atoms of each pairs range from 3.43(1) to 3.50(1) Å and are indicative of the spacing of the anthracenyl groups within a stack. Examination of the literature indicates that offset structures in organic π–π-stacks have been predicted to be energetically favorable [11]. It must be pointed out that, in the present case, the slippage of the anthracenyl ligands leads to an optimal positioning of the mercury atom which forms intermolecular contacts with a neighboring chlorine atom and a neighboring anthracenyl ligand (Fig. 3). The resulting intermolecular Hg(1b)···Cl(1a) distance of 3.311(2) Å is slightly shorter than the sum of the van der Waal's radii (r_{vdw} (Cl) = 1.8 Å [12], r_{vdw} (Hg) = 1.73 Å [13]) and supports the pres-

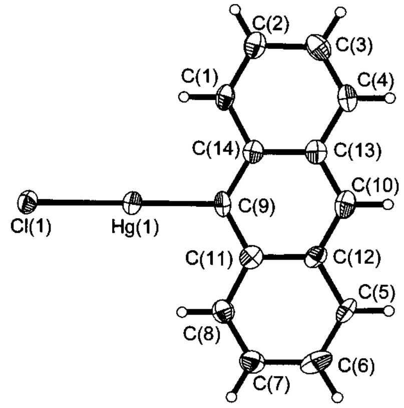

Fig. 1. ORTEP drawing (50%) of a monomer of **1** in the crystal. Selected bond lengths (Å) and angles (°): Hg(1)–C(9) 2.070(8), Hg(1)–Cl(1) 2.337(2); C(9)–Hg(1)–Cl(1) 175.4(2).

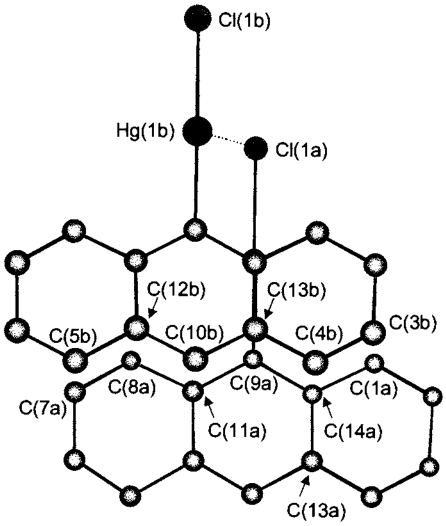

Fig. 2. Ball and stick diagram of two monomeric units of polymeric **1**. The slippage of the anthracenyl group is evident from this view. Selected interatomic distances (Å) and angles (°). C(5b)–C(7a) 3.50(1), C(12b)–C(8a) 3.50(1), C(10b)–C(11a) 3.48(1), C(13b)–C(9a) 3.44(1), C(4b)–C(14a) 3.44(1), C(3b)–C(1a) 3.47(1); C(12b)–C(10b)–C(11a) 87.7(5), C(13b)–C(10b)–C(11a) 85.3(5), C(9a)–C(14a)–C(4b) 91.5 (6), C(13a)–C(14a)–C(4b) 84.6 (5), C(1a)–C(14a)–C(4b) 95.1(6).

ence of a weak interaction [14]. Similarly, the Hg···C distances of 3.388(7) Å (Hg(1a)···C(1b)), 3.349(8) Å (Hg(1a)···C(14b)) and 3.483(8) Å (Hg(1a)···C(9b)) indicate the presence of a trihapto-π-interaction between the mercury center and a neighboring anthracenyl ligand. These Hg···C intermolecular distances are typical from systems featuring such linkages [3,15] and can be compared to the value of 3.45 Å measured in the structure of tetrameric 2-pyridylphenylmercurychloride [16].

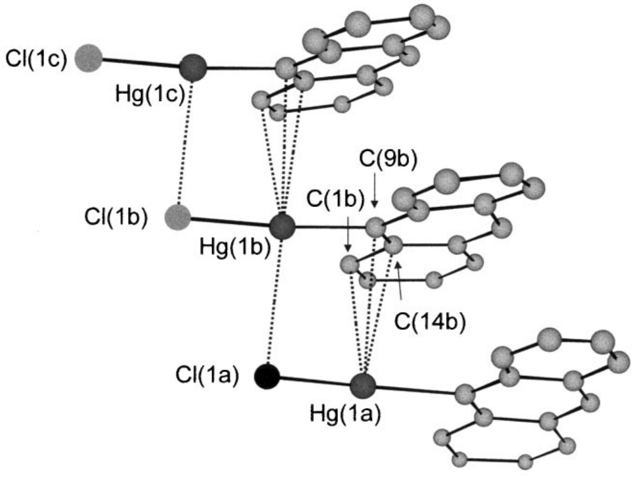

Fig. 3. Ball and stick diagram of three monomeric units of polymeric **1**. The Hg···Cl and Hg···C contacts are represented by dotted lines. Selected lengths (Å) and angles (°): Hg(1b)–Cl(1a) 3.311(2), Hg(1a)–C(1b) 3.388(7), Hg(1a)–C(14b) 3.349(8), Hg(1a)–C(9b) 3.483(8); Cl(1a)–Hg(1b)–C(14c) 157.2(2), Cl(1a)–Hg(1b)–C(1c) 136.3(3), Cl(1a)–Hg(1b)–C(9c) 90.90(6).

The supramolecular structure of **1** can be regarded as molecular stairs cemented by a combination of π–π-stacking, Hg···Cl and Hg···π-system interactions. It thus differs from the structure of chloromercuriobenzene which forms a ladder polymer in which the monomeric units are connected by head to tail Hg_2Cl_2 bridges [17].

3. Experimental

3.1. General consideration

Nuclear magnetic resonance spectra were obtained on a JEOL-GX 400 instrument (400 MHz for ^{1}H, 100.5 MHz for ^{13}C, 71.56 MHz for ^{199}Hg). All spectra were recorded in DMSO-d_6. Neat $HgMe_2$ was used as an external standard for the ^{199}Hg-NMR spectra. The proton and carbon signals of the deuterated solvent were used as internal standard for the ^{1}H- and ^{13}C-NMR spectra, respectively. The fluorescence spectra were recorded in KBr pellets with a Perkin–Elmer LS 50 B luminescence spectrometer. Mass spectra were recorded using a Finnigan MAT 90 spectrometer. The laboratory for microanalysis at Technische Universität München performed the elemental analyses. All experiments were carried out under a dry inert atmosphere of N_2 using standard Schlenk technique or a glove box (Labmaster 130, Fa. M. Braun). All melting points were measured on samples in sealed capillaries and are uncorrected. THF and hexane were dried over Na/K and distilled prior to use. All other solvents were used without further purification. All commercially available starting materials were purchased from Aldrich Chemicals and used as provided. 9-Lithio-anthracene [18] and 9,10-dilithio-anthracene [19] were prepared according to the published procedure.

3.2. 9-Chloromercurio-anthracene (**1**)

tert-Butyllithium (18 mmol, 12 ml, 1.5 M solution in hexane) was added dropwise to a stirred suspension of 9-bromoanthracene (2.31 g, 9 mmol) in THF (70 ml) at −78°C. The solution was allowed to warm to room temperature (r.t.) and was then stirred for an additional 2 h. The resulting suspension was carefully added to a vigorously stirred solution of $HgCl_2$ (36 mmol, 9.76 g) in THF (70 ml) at 0°C via a cannula. After complete addition the yellow reaction mixture was stirred at r.t. for 2 h. Slow addition of water (200 ml) lead to the precipitation of the product which was isolated by filtration, washed three times with water (50 ml) and twice with THF (20 ml). After drying, the product was dissolved in DMF (60 ml) and placed in a crystallization dish. Slow evaporation of the solvent afforded a

77% yield (2.86 g) of compound **1** (dec. 180°C). NMR data for **1** (25°C). ^{1}H-NMR: δ 7.54 (m, 4 H, H-2/3/6/7), 8.09 (d, $^3J_{H,H} = 8.0$ Hz, 2 H, H-1/8), 8.27 (d, $^3J_{H,H} = 8.0$ Hz, 2 H, H-4/5), 8.55 (s, 1 H, H-10). ^{13}C-NMR: δ 125.8, 126.2 (C-2/3/6/7), 127.4 (C-4a/5a), 128.9 (C-10), 132.3, 132.5 (C-1/4/5/8), 136.6 (C-1a/8a), 156.8 (C-9). ^{199}Hg-NMR: δ -1100. Calc. for $C_{14}H_9HgCl$: C, 40.7; H, 2.2. Anal. Found: C, 40.0; H, 2.2. The low carbon content found is due to the presence of finally divided mercury metal in the sample. Mass spectrum (CI, isobutane): 414 (M^+, 56.3%), 178 ($C_{14}H_{10}$, 100%).

3.3. *9,10-Bis(chloromercurio)-anthracene* (**2**)

tert-Butyllithium (36 mmol, 24 ml, 1.5 M solution in hexane) was added dropwise to a stirred suspension of 9,10-dibromoanthracene (3.0 g, 9 mmol) in THF (60 ml) at -78°C. The reaction mixture was allowed to warm slowly to r.t. and then was stirred for an additional 2 h. The resulting suspension was carefully added to a vigorously stirred solution of $HgCl_2$ (72 mmol, 19.5 g) in THF (50 ml) at 0°C via a cannula. After complete addition the bright yellow reaction mixture was stirred at r.t. for 1 h and then refluxed for 8 h. The insoluble product was isolated by filtration and washed three times with water (25 ml) and twice with THF (10 ml). Following drying under vacuum, **2** can be obtained as a bright yellow solid in a 82% yield (4.79 g) (m.p. = 360°C). Anal. Calc. for $C_{14}H_8Hg_2Cl_2$: C, 25.92; H, 1.23. Found: C, 25.98; H, 1.36. NMR data for **2** (100°C). ^{1}H-NMR: δ 7.62 (m$_c$, 4 H, H-1/4/5/8), 8.29 (m$_c$, 4 H, H-2/3/6/7). ^{13}C{^{1}H}-NMR: δ 125.1 (C-2/3/6/7), 131.8 (C-1/4/5/8), 136.6 (1a/8a/4a/5a), (C-9/10) not detected. Mass spectrum (CI, isobutane): 648 (M^+, 5.6%), 202 (Hg, 46.7%), 178 ($C_{14}H_{10}$, 100%).

3.4. *Structural study of* **1**

X-ray data for **1** were collected at -100°C on a Siemens SMART-CCD diffractometer using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). A colorless plate of **1** ca. $0.10 \times 0.11 \times 0.02$ mm^3 in size was selected and mounted on a glass fiber with epoxy. The data were collected using 0.3°-wide ω-scans with a crystal to detector distance of 5.0 cm to yield a complete (99.3%) sphere of 12483 (2719 unique, $R_{int} = 0.0531$) data ($4.68 \leq 2\theta \leq 56.52$°). The data were corrected for absorption empirically on the basis of equivalent reflection measurements using the SADABS routine [20] ($T_{max} = 0.6471$, $T_{min} = 0.3939$). Other key crystallographic parameters are as follows: $C_{14}H_9ClHg$, $M = 413.25$, orthorhombic space group $Pca2_1$; $a = 15.8079(1)$, $b = 4.0830(1)$, $c = 17.4121(2)$ Å; $V = 1123.841(15)$ Å^3; $Z = 4$; $\mu = 13.897$ mm^{-1}. The structure was solved by direct method and refined by full-matrix least-squares against F^2 using the SHELXTL/PC (ver. 5.03) package. The refinement converged with residuals [21] of R_1 (wR_2) = 0.0326 (0.0628) for 145 refined parameters and 2212 reflections with $I > 2\sigma(I)$.

4. Supplementary material

The complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 103303 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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[21] $R_1 = \Sigma|F_o - F_c| = \Sigma F_o$; $wR_2 = \{\Sigma w|F_o^2 - F_c^2|^2 = \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2\ (F_o^2) = (aP)^2 = bP]$ with $P = [2F_c^2 = \mathrm{Max}(F_o^2{,}0)]/3$ and a and b are fitted parameters.