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Journal of Organometallic Chemistry 515 (1996) 259–260

Journal of Organometallic Chemistry

Preliminary communication

Bis(4-pyridylethynyl)mercury

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Received 11 December 1995

Abstract

4-Ethynylpyridine reacts with mercuric acetate to yield bis(4-pyridylethynyl)mercury whose X-ray crystal structure reveals infinite zigzag chains in which the metal has a T-shaped coordination geometry consisting of two ethynyl groups attached at close distances in an approximately linear fashion, the pyridine of a neighbouring molecule providing the third and distinctly longer coordinate bond approximately perpendicular to the other two.

Keywords: Mercury; Ethynyl; Crystal structure

As part of a wide ranging study of infinite framework structures constructed from metal-bridging 2-connecting units favouring an approximately linear disposition such as cyanide [1], 4,4'-bipyridine [2] and 1,4-bis(4-pyridyl)butadiyne [3], an investigation was initiated into the structural chemistry of metal derivatives of 4-ethynylpyridine. Reported here are the synthesis and X-ray crystal structure of its mercury(II) derivative bis(4-pyridylethynyl)mercury, **1**.

Colourless needle-like crystals of **1** were obtained from a solution of mercuric acetate dissolved in 1-butanol/acetic acid combined with a solution of 4-ethylnylpyridine in methanol (Found: C, 41.4; H, 1.8; N, 7.1. $C_{14}H_8HgN_2$ requires C, 41.6; H, 2.0; N, 6.9%). Although the crystals directly obtained in this way were of sufficient quality to give X-ray diffraction data, better crystals for use in the analysis below [4] were obtained by recrystallisation from dimethylformamide solution.

The structural analysis revealed the mercury coordination environment shown in Fig. 1, all metal centres being equivalent. Selected interatomic distances and angles are provided with Fig. 1. Both terminal ethynyl carbon atoms of the two ethynylpyridine units are coordinated at a Hg–C distance of 2.02(3) Å with approximate linearity at the metal and at all four ethynyl carbon centres.

Fig. 2 shows the extended structure within the crystal, each molecule of **1** is attached to two neighbours by elongated Hg–N bonds (2.64(3) Å) all of which are equivalent, whereby infinite zigzag polymeric chains are produced. The resulting coordination geometry can

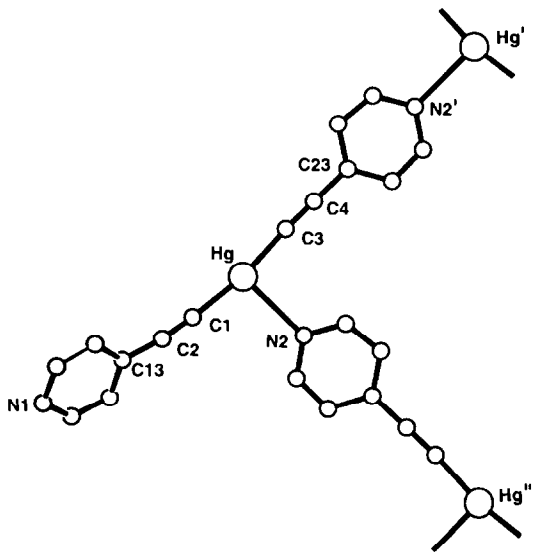

Fig. 1. Repeat unit of the polymer bis(4-pyridylethynyl)mercury and the T-shaped geometry of the metal atom. Selected bond distances and angles: Hg–N2 2.64(3), Hg–C1 2.02(3), Hg–C3 2.02(3), C1–C2 1.19(4), C3–C4 1.17(4), C2–C13 1.50(4), C4–C23 1.47(4) Å; C1–Hg–C3 172(1), N2–Hg–C1 96(1), N2–Hg–C3 91(1), Hg–C1–C2 166(3), Hg–C3–C4 171(3), C1–C2–C13 178(3), C3–C4–C23 178(3)°.

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Elsevier Science S.A.
SSDI 0022-328X(96)06185-2

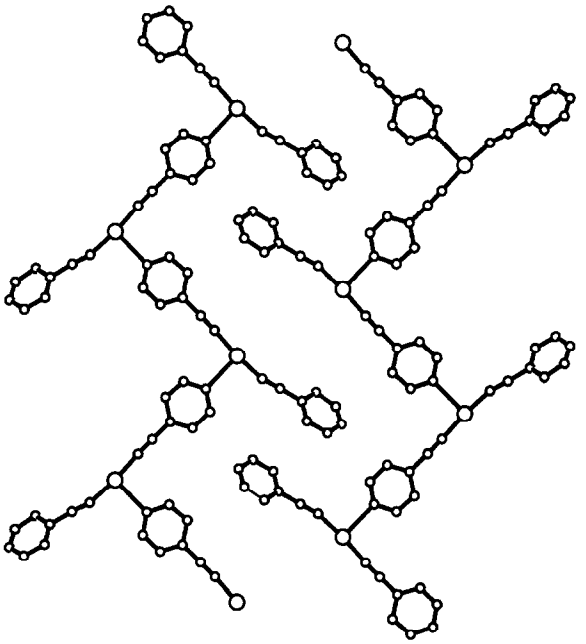

Fig. 2. Zigzag chain structure of bis(4-pyridylethynyl)mercury.

be described as T-shaped. One pyridine nucleus from each molecule of **1** remains uncoordinated and fits snugly into an indentation formed by a neighbouring zigzag chain.

Coordination environments involving some short metal–ligand bonds together with some that are distinctly longer are not uncommon in mercury(II) derivatives [5]. For example, a T-shaped coordination geometry similar to that described here is seen in 2(pyridin-2'-yl)phenylmercuric chloride [6] in which the phenyl and chloro ligands are bound in an approximately linear fashion at close distances and the pyridine is attached more weakly (Hg–N, 2.63(1) Å) approximately at right angles to the other two ligands.

We are presently exploring the potentialities of **1** itself as an unusually long "linear" 2-connector capable in principle of binding metal centres separated by the order of 18 or 19 Å.

Acknowledgement

We are grateful for support from the Australian Research Council.

References and notes

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[4] Crystal data: $Hg(C_7H_4N)_2$; M, 404.8; monoclinic; space group, $P2_1/c$ (No. 14); $a = 4.137(2)$; $b = 26.559(9)$; $c = 11.088(2)$ Å; $\beta = 91.68(3)°$; $V = 1218(1)$ Å^3; $Z = 4$, $D_{meas} = 2.20$ g cm^{-3} and $D_{calc} = 2.207$ g cm^{-3}; $\lambda = 0.71073$ Å; $\mu = 125.9$ cm^{-1}; $F(000) = 744$; $T = 293(1)$ K; crystal dimensions $0.38 \times 0.038 \times 0.05$ mm^3; maximum residual electron density 2.66 e Å^{-3}. Data were measured for 2265 reflections using an Enraf-Nonius CAD 4F diffractometer ($2 < 2\theta < 40°$) yielding 1578 unique reflections; R_{merg} 0.0253. The structure was solved and refined using SHELXS86 (G.W. Sheldrick, 1985) and SHELX76 (G.M. Sheldrick, 1976) respectively employing data corrected for absorption; R and R_w 0.056 and 0.054 respectively for 782 reflections with $I > 2\sigma(I)$. Tables of atomic coordinates, interatomic distances, angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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