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Letter

First structurally characterised metal complex of a 2*H*-benzimidazole derivative. Copper mediated synthesis of 2,2-dimethyl-2*H*-benzimidazole from 1,2-phenylenediamine and acetone

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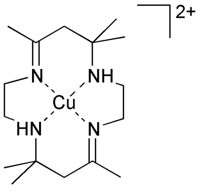
2,2-Dimethyl-2*H*-benzimidazole (1) was synthesised by exploiting the reaction of acetone with bis(1,2-phenylenediamine)copper(II) perchlorate. Additionally, the X-ray crystal structure of $[Cu^I(1)(PPh_3)_2]ClO_4$ is reported.

2*H*-Benzimidazole is a tautomer of 1*H*-benzimidazole and has an *ortho*-quinonoid electronic structure. Our AM1 calculations[1] using the standard MOPAC package (version 1.1) shows that in the gas phase 2*H*-benzimidazole is energetically less stable than 1*H*-benzimidazole by 27.5 kcal mol^{-1}. While 1*H*-benzimidazole is not a rare ligand in transition metal chemistry, nothing is known about the metal binding of 2*H*-benzimidazole. Herein we describe, for the first time, two copper(I) complexes of the 2,2-dimethyl derivative of 2*H*-benzimidazole. The structure of one of them has been determined. We also describe a novel viable synthesis of 2,2-dimethyl-2*H*-benzimidazole (**1**).

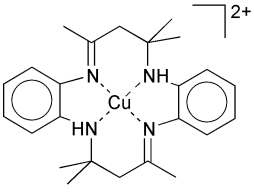
Reaction of acetone with bis(ethylenediamine)copper(II) perchlorate gives rise to the cationic copper(II) complex of Curtis' macrocycle **A**.[2] In an attempt to generate **B**, the 1,2-phenylenediamine (OPDA *i.e. ortho*-phenylenediamine) counterpart of **A**, which is not yet known, we have reacted acetone with $Cu(OPDA)_2(ClO_4)_2$. It is found that this reaction in air at room temperature does not yield **B**; it leads instead to a reddish-brown copper(I) complex of **1** of the formulation $Cu(\mathbf{1})ClO_4$ (**2**), sparingly soluble in acetone, in almost quantitative yield and from the filtrate is obtained the perchloric acid salt[3,4] of 2,3-dihydro-2,2,4-trimethyl-1*H*-1,5-benzodiazepine (**3**) in *ca.* 35% yield (eqn. 1).

$$[Cu(OPDA)_2](ClO_4)_2 + \text{acetone} \rightarrow$$
$$\mathbf{2} + 0.5\,H_2 + H^+ + OPDA + ClO_4^- \tag{1a}$$
$$H^+ + OPDA + ClO_4^- + 2\ \text{acetone} \rightarrow \mathbf{3}\cdot HClO_4 \tag{1b}$$

Later we have found that reaction 1 also occurs in the absence of air. Complex **2** is stable in air in the solid state for about two weeks. However, in methanol **2** is stable in air for about 2 h only; on standing in air, the reddish-brown colour of the methanol solution slowly disappears becoming almost colourless. The identity of the organic fragment in **2** is corroborated by the X-ray crystal structure (Fig. 1) of $[Cu(\mathbf{1})(PPh_3)_2]ClO_4$ (**4**), which is obtained by the smooth reaction of PPh_3 with **2** at room temperature in a 2 : 1 molar ratio in methanol.



A



B

Complex **4** is indefinitely stable in air in the solid state as well as in solution. As revealed by the X-ray crystal structure, the copper(I) centre in **4** has a trigonal NP_2 coordination sphere with the interligand angles very close to 120°. The coordination sphere in most tricoordinate copper(I) complexes is found to be somewhat T-shaped. For an example, see ref. 5. Fig. 1 describes the first structurally characterised metal complex of a 2*H*-benzimidazole. It is noted that the corresponding 1*H*-benzimidazole complex is not known. Our bond valence sum calculations[6,7] show that the Cu–N bond distance [1.997(3) Å] in **4** is quite close to that expected (1.98 Å) for a symmetric CuN_3^+ moiety. In this context, we mention that while some 2,2-dialkyl derivatives of 2*H*-imidazole are known,[8] no metal complexes have so far been reported.

Interestingly, when OPDA is refluxed in acetone, one obtains 2-methyl-2-isobutenylbenzimidazoline.[9] On the other hand, reaction of acetone with OPDA at room temperature in

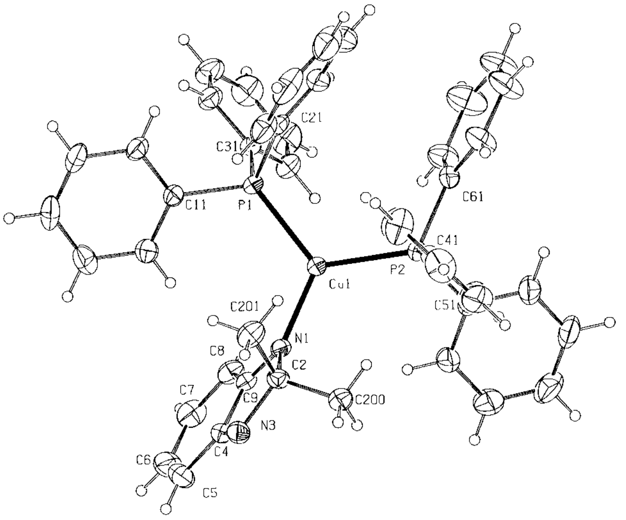


Fig. 1 The structure of the cation in **4** with ellipsoids at 30% occupancy. Selected bond distances (Å) and angles (°): Cu1–N1 1.997(3), Cu1–P1 2.287(3), Cu1–P2 2.280(2), N1–C2 1.499(5), C2–N3 1.469(5), N3–C4 1.286(5), C4–C5 1.453(6), C5–C6 1.326(7), C6–C7 1.436(7), C7–C8 1.364(7), C8–C9 1.425(6), C9–N1 1.308(5), C4–C9 1.469(5); N1–Cu1–P1 118.09(12), N1–Cu1–P2 119.83(11), P1–Cu1–P2 120.00(4).

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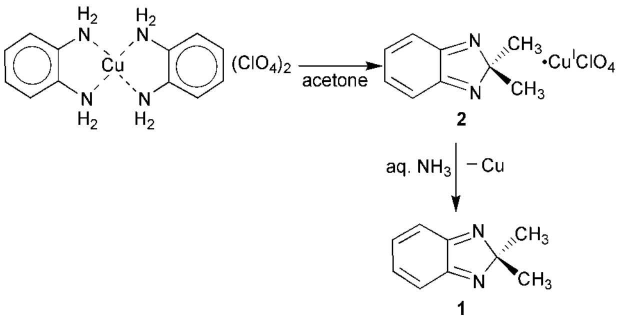

Scheme 1

the presence of an acid gives the acid salt of **3**.[3,4] Thus, the copper atom clearly plays an important role in the formation of **1** here. Since reaction 1 also occurs in an N_2 atmosphere, we can say that copper(II) acts as a one-electron oxidant in reaction 1 and it is not a case[10–12] of copper-mediated aerial oxidation.

Demetallation of **2** by aqueous ammonia affords **1** in the free state. The overall synthetic procedure is summarised in Scheme 1. The overall yield of **1** in Scheme 1 is *ca.* 60%. Compound **1** is a light reddish-brown liquid. Its ^1H and ^{13}C NMR spectra in a 4 : 1 $CDCl_3$–CCl_4 mixture (Fig. 2) show that **1** has a C_2 axis, as expected. It is extremely unstable in air; it rapidly turns red and solidifies with decomposition. From the decomposed red solid, crystals of OPDA can be isolated by trituration with hot hexane (65–70 °C fraction from petroleum). Previously, **1** has been synthesised by reacting benzofurazan *N*-oxide with 2-nitropropane under basic catalysis, followed by reduction of the resulting 2,2-dimethyl-2*H*-benzimidazole bis-*N*-oxide with $NaBH_4$.[13,14] However, this procedure is not straightforward and the overall yield was not reported. Moreover,[13,14] **1** had not been fully characterised.

Because of "blocked tautomerisation", 2,2-dimethyl-2*H*-benzimidazole is more stable than 2*H*-benzimidazole towards tautomerisation. Our AM1 calculations show that **1** is energetically less stable than its 1*H* tautomer by only 15.6 kcal mol^{-1}. This indicates, within the framework of the AM1 method, a gain of 11.9 kcal mol^{-1} in stability for **1** towards tautomerisation in comparison with 2*H*-benzimidazole.

Thus, we have found a new and easy synthesis of 2,2-dimethyl-2*H*-benzimidazole (**1**) that exploits the reaction between acetone and bis(1,2-phenylenediamine)copper(II) perchlorate. Though in the free state **1** is very unstable in air, it becomes quite stable in air upon binding copper(I). At present we are engaged in an examination of the generality of Scheme 1 and in developing the transition metal chemistry of 2*H*-benzimidazole.

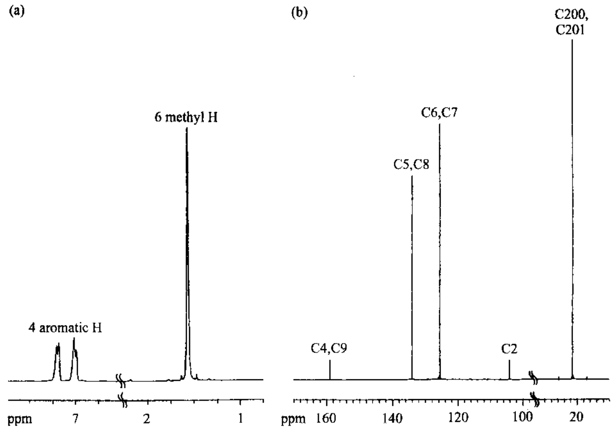

Fig. 2 (a) ^1H and (b) ^{13}C NMR spectra (300 MHz; TMS reference) of **1** in a 4 : 1 $CDCl_3$–CCl_4 mixture. For the labelling scheme of the C atoms, see Fig. 1.

Experimental

Syntheses

Reaction 1. Silky violet $Cu(OPDA)_2(ClO_4)_2$ (3 g, 6.27 mmol), prepared by a reported procedure,[15] was suspended in 75 ml of purified acetone and stirred for 6 h at room temperature with a $CaCl_2$ (fused) guard tube fitted to the reaction vessel. The reaction mixture gradually turned intense red during stirring. The reddish-brown Cu(**1**)ClO_4 (**2**) that appeared was filtered off, washed thoroughly with acetone and dried *in vacuo* over fused $CaCl_2$; yield: 1.9 g (93%). Anal. calc. for $C_9H_{10}ClCuN_2O_4$: C, 34.94; H, 3.26; N, 9.06; Cu, 20.55%. Found: C, 34.90; H, 3.30; N, 9.01; Cu, 20.49%. FTIR (KBr): ν 1620s,br (C=N), 1135vs, 1100vs, 1070vs (ClO_4) cm^{-1}. Diamagnetic: Λ_M (CH_3OH) 83 $cm^2\ \Omega^{-1}\ mol^{-1}$ (1 : 1 electrolyte). UV-VIS (nujol): λ_{max} 460, 358, 280 nm. UV-VIS (CH_3OH; $c = 0.50 \times 10^{-3}$ mol dm^{-3}): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 414 (1200), 352 (2800), 270 (3300), 218 (8100) nm. ^1H NMR (300 MHz, $(CD_3)_2SO$, TMS): δ 1.57 (s, methyl, 6H), 7.29–7.36 (br, m, phenyl, 4H). ^{13}C NMR (300 MHz, $(CD_3)_2SO$, TMS): δ 22.71, 104.54, 124.87, 137.06, 159.27.

The filtrate obtained after the isolation of **2** was evaporated on a water bath to obtain a dark mass. It was dissolved in 10 ml of hot water and filtered. To the red filtrate, cooled to room temperature, a saturated aqueous solution of $NaClO_4 \cdot H_2O$ was added dropwise with stirring until a crystalline precipitate started to appear. The reaction mixture was left in air for 1 h. The deposited orange-red diamond-like crystals were filtered off, washed with 5 ml of cold water and dried *in vacuo* over fused $CaCl_2$; yield: 0.6 g (34%). The crystals were characterised as **3** · $HClO_4$.[3,4]

[Cu(1)(PPh$_3$)$_2$]ClO$_4$ (4). To a suspension of 0.32 g (1 mmol) of **2** in 15 ml of methanol, 0.52 g (2 mmol) of PPh_3, dissolved in 20 ml of methanol, was added dropwise with constant stirring to obtain a clear yellowish-orange solution. The reaction mixture was left in air overnight. The yellowish-brown compound **4** that precipitated was filtered off, washed with 5 ml of cold methanol and dried *in vacuo* over fused $CaCl_2$; yield: 0.45 g (54%). An additional crop of crystals could be obtained by adding diethyl ether to the filtrate. Anal. calc. for $C_{45}H_{40}ClCuN_2O_4P_2$: C, 64.80; H, 4.84; N, 3.36; Cu, 7.62%. Found: C, 64.72; H, 4.92; N, 3.36; Cu, 7.67%. FTIR (KBr): ν 1610s,br (C=N), 1150–1075vs,br (ClO_4) cm^{-1}. Diamagnetic: Λ_M (CH_3OH) 91 $cm^2\ \Omega^{-1}\ mol^{-1}$ (1 : 1 electrolyte). UV-VIS (nujol): λ_{max} 465, 360, 290 nm. UV-VIS (CH_3OH; $c = 0.05 \times 10^{-3}$ mol dm^{-3}): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 345 (7050), 250 (25 800), 222 (66 900) nm. ^1H NMR (300 MHz, $(CD_3)_2SO$, TMS): δ 1.37 (s, methyl, 6H), 7.07–7.50 (br, m, phenyl, 34H). ^{13}C NMR (300 MHz, $(CD_3)_2SO$, TMS): δ 22.05. 104.66, 125.83, 129.27, 129.41, 130.76, 132.42, 132.98, 133.86, 135.73, 159.33.

2,2-Dimethyl-2*H*-benzimidazole (1). **2** (3 g, 9.3 mmol) was taken up in 75 ml of chloroform and stirred for 5 min. To the resulting dark brown suspension, 50 ml of 25% aqueous ammonia was added and stirred for 1 h at room temperature, after which it was filtered. The blue aqueous layer of the filtrate was discarded. The light reddish-brown layer of the filtrate was collected and evaporated at room temperature under reduced pressure to *ca.* 5 ml, which was then loaded on a neutral alumina column (25 × 2.5 cm) and eluted with a 1 : 9 diethyl ether–petroleum ether mixture. The yellowish fraction (*ca.* 200 ml) was collected, which upon removal of the solvent at room temperature under reduced pressure yielded **1** as a light reddish-brown liquid. (The whole process was completed within 8 h). Yield: 0.9 g (63%). Anal. calc. for $C_9H_{10}N_2$: C, 73.93; H, 6.90; N, 19.16%. Found: C, 73.91; H, 6.88; N, 19.13%. Density: 0.93 g cm^{-3}. EI-MS: *m*/*z* 146.1 ($\mathbf{1}^+$, 100), 131.1 ($\mathbf{1}^+ - CH_3$, 90), 105.1 ($\mathbf{1}^+ - C_3H_5$, 28), 90.1

($\mathbf{1}^+ - NC_6H_3$, 42), 78.1 ($C_6H_6^+$, 12), 63.0 ($C_5H_3^+$, 6), 51.0 ($C_4H_3^+$, 8), 41.0 ($C_3H_5^+$, 15%). UV-VIS (CH_3OH): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 354 (2500), 263 (2800), 217 (6000) nm. ^{1}H NMR (300 MHz, $CDCl_3$–CCl_4, TMS): δ 1.54 (s, methyl, 6H), 6.99–7.02 (br, phenyl, 2H), 7.18–7.21 (br, phenyl, 2H). ^{13}C NMR (300 MHz, $CDCl_3$–CCl_4, TMS): δ 21.33, 104.14, 125.69, 134.06, 159.04. All studies on **1** were done with freshly prepared samples.

X-Ray crystallography

Single crystals of **4**, which are yellowish-brown in colour, were obtained by indirect diffusion of diethyl ether into a moderately concentrated dichloromethane solution of the complex. The data were collected with Mo-Kα radiation using the MARresearch Image Plate system at 293(2) K. The structure was refined on F^2 using SHELXL-93.[16] Final residuals: $R_1 = 0.0599$ and $wR_2 = 0.1591$ for 5304 reflections with $I \geqslant 2\sigma(I)$; $R_1 = 0.0907$ and $wR_2 = 0.1775$ for all data.

Crystal data. $C_{45}H_{40}ClCuN_2O_4P_2$ (**4**): $M_w = 833.72$, monoclinic, space group $C2/c$, $a = 39.72(4)$, $b = 10.198(13)$, $c = 24.59(3)$ Å, $\beta = 123.78(1)°$, $U = 8280(16)$ Å^3, $Z = 8$, $\mu = 0.714$ mm^{-1}, 12 812 reflections collected, 7360 independent, $R_{int} = 0.0289$.

CCDC reference number 440/235. See http://www.rsc.org/suppdata/nj/b0/b007410l/ for crystallographic files in .cif format.

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