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Synthesis, structures and reactivity of *N*-donor-functionalised Cu(I) aryloxides

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Abstract

The preparation and characterisation of the Cu(I) aryloxides $[Cu_{16}(3-pyO)_{16}(dppm)_8](1), [\{Cu_2(2-pyO)_2(dppm)\}_2](2)$ and $[\{Cu_3(\mu_3-6-OQ)_2(dppm)_3\}\{(6-HOQ)_2(\mu-6-OQ)\}](3)$ (dppm = 1,2-bis-diphenylphosphinomethane, 6-HOQ = 6-hydroxyquinoline, py = pyridine) are described. A first attempt to employ organic anhydrides in insertion reactions with Cu(I) aryloxides was made producing the one-dimensional coordination polymer $1/_{\infty}[Cu_3(3-pyO)(CO_2C_2H_4Boc)(dppm^-)(dppm)]_{\infty}$ (4) (Boc = *tert*-butoxycarbonyl). © 2005 Elsevier B.V. All rights reserved.

Keywords: Metal alkoxide; Organic anhydride; Insertion reaction

1. Introduction

Insertion reactions of organic anhydrides into the metal–oxygen bond of late transition metal alkoxides could provide a new route to inorganic/organic hybrid materials with possible applications, e.g., as storage devices for gases or matrices for catalytic transformations [1–4]. As a model reaction we have recently described the insertion reaction of various organic anhydrides into the Cu–O bond of [CuO'Bu], producing Cu(I) carboxylate complexes when performed at low temperature or in the presence of tertiary phosphine ligands (Scheme 1) [5,6].

Metathesis reactions of Cu(I) complexes obtained in these reactions with transition metal halides offer access to a large number of compounds [6] which can subsequently be tested for physical properties desirable for a specific inorganic/organic hybrid material (see Scheme 2).

In addition to the choice of anhydride and metal atom a further modification of the synthetic approach represents the use of a variety of Cu(I) alkoxides or aryloxides. In order to construct complex metal organic aggregates by insertion reactions we therefore set out to synthesise a variety of Cu(I) aryloxides containing hydroxypyridines and hydroxyquinolines as *N*-heterocyclic substituents and probe their reactivity with organic anhydrides. These efforts complement synthetic investigations of Cu(I) aryloxides with nitrogen donor atoms centres similar to that of copper(I) complexes of 6-methyl-2-hydroxypyridine and 6-hydroxy-2,2'-bipyridine [7–9] and represent a step in the ongoing development of insertion reactions as a new route to inorganic/organic hybrid materials. Here we report the synthesis and structural characterisation of three new Cu(I) aryloxides and the first results of subsequent reactions with organic anhydrides.

2. Experimental

2.1. General remarks

All operations were carried out in an atmosphere of purified argon. Solvents were dried over sodium/benzophenone. Maleic anhydride was recrystallised from diethyle-ther. Chemicals were purchased from Aldrich. [CuO'Bu] was prepared according to a published procedure [10].

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Scheme 1. Insertion reaction of organic anhydrides into the Cu–O bond of Cu(I) alkoxides R, R' = alkyl.

$$Cu_{O} \xrightarrow{O} R' + MX \longrightarrow M_{O} \xrightarrow{O} R' + CuX$$

Scheme 2. Metathesis reactions of Cu(I) complexes obtained from insertion reactions (M = metal).

1. To a solution of 0.14 g of (1.00 mmol) [CuO^tBu] in 10 mL THF was added a solution of 0.10 g (1.00 mmol) 3hydroxypyridine in 5 mL THF. After stirring the reaction mixture for 30 min at RT, a colourless precipitate was formed and dissolved upon addition of a solution of 0.20 g (0.50 mmol) dppm in 5 mL THF. The reaction was filtered and the yellow filtrate concentrated to approximately 3 mL. Addition of 1 mL hexane and storage of the solution at -20 °C for 2 days produced colourless crystals of 1. Yield 0.38 g, 90%; m.p. 209 °C; Calc. for C280H240Cu16N16O16P16 (corresponding to loss of lattice THF): C, 60.0; H, 4.3; N, 4.0. Found: C, 59.0; H, 4.3; N, 4.0%. IR (KBr) $v_{\text{max}}/\text{cm}^{-1} = 1564$, 1544 (C–N), 1468 (P– C); δ_P (CDCl₃, 25 °C, 161.96 MHz, 85% H₃PO₄) -13,0 (br s, PPh); $\delta_{\rm H}$ (400 MHz, CDCl₃, 25 °C, TMS) 8.1–6.9 (m, 24 H ar., Ph and py), 3.8, 1.8 (m, 4H, thf), 3.2 (br s, 2H, CH₂PPh₂), $\delta_{\rm C}$ (400 MHz, CDCl₃, 25 °C, TMS), 132.9–128.5 (C ar.), 68.0, 25.6 (s, thf), 34.1 (s, CH₂PPh₂).

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Table	

Details of the X-ray data collection and refinemer	nts
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2. 2 was synthesised analogously to 1 with the exception that 2-hydroxypyridine was used in place of 3-hydroxypyridine. Storage of the solution for two days in RT produced colourless crystals of 2. Yield 0.29 g, 68%; m.p. 275 °C; Calc. for $C_{70}H_{60}Cu_4N_4O_4P_4$ (excluding lattice-bond THF): C, 60.0; H, 4.3; N, 4.0. Found: C, 59.7; H, 4.3; N, 3.8%. IR (CsI, nujol) $v_{max}/cm^{-1} = 1586$ (C–N), 1465 (P– C); δ_P ([D₆]DMSO, 25 °C, 161.96 MHz, 85% H₃PO₄), -11.2 (br s, PPh); δ_H (400 MHz, [D₆]DMSO, 25 °C, TMS), 8.6–6.9 (m, 26H , H ar.), 3.6 (m, 4H, thf), 1.8 (m, 4H, thf), 3.3 (br. s, 2H, CH₂PPh₂); δ_C (400 MHz, [D₆]DMSO, 25 °C, TMS), 133.0–127.9 (C ar.), 67.0, 25.1 (s, thf), 27.8 (s, CH₂PPh₂).

3. To a solution of 0.14 g (1.00 mmol) [CuO^tBu] in 5 mL THF was added a solution of 0.15 g (1.00 mmol) 6hydroxyquinoline in 10 mL THF. The solution was stirred for 2 h resulting in the formation of a colourless precipitate. After addition of a solution of 0.40 g (1.00 mmol) dppm in 5 mL THF the reaction was filtered and the brown filtrate concentrated to approximately 5 mL. Addition of 1 mL hexane and storage of the solution at -40 °C for one week produced colourless crystals of 3. Yield 0.45 g, 68%; m.p. 206 °C; Calc. for C471H385Cu12N19O19P24 (corresponding to loss of lattice THF): C, 69.7; H, 4.8; N, 3.3. Found: C, 68.9; H, 4.8; N, 3.2. IR (KBr) v_{max}/ $cm^{-1} = 3456$ (OH), 1605, 1579 (C–N), 1462 (P–C); δ_P ([D₆]DMSO, 25 °C, 161.96 MHz, 85% H₃PO₄) -13.0 (br s, PPh), $\delta_{\rm H}$ (400 MHz, [D₆]DMSO, 25 °C, TMS) 8.8– 6.8 (m, 26H, ar.), 3.6, 1.7 (m, 4H, thf), 3.4 (br. s, 2H, CH_2PPh_2), δ_C (400 MHz, [D₆]DMSO, 25 °C, TMS) 132.8-127.9 (C ar.), 67.0, 25.1 (s, thf), 30.9 (s, CH₂PPh₂).

Compound	1	2	3	4
Formula	$C_{422}H_{526}Cu_{16}N_{16}O_{50}P_{16}$	C78H76Cu4N4O6P4	$C_{591}H_{625}Cu_{12}N_{19}O_{49}P_{24}$	C ₇₄ H ₈₀ Cu ₃ NO _{7.5} P ₄
Formula weight	8134.75	1543.47	10284.00	1417.89
<i>T</i> (K)	203(2)	173(2)	120(2)	120(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	C2/c
a (Å)	20.5768(10)	11.0458(12)	14.489(3)	44.249(3)
b (Å)	21.3764(9)	12.6158(15)	28.050(3)	14.0383(7)
c (Å)	24.7779(11)	12.8624(9)	32.873(3)	25.1116(15)
α (°)	74.857(3)	92.870(8)	101.811(6)	90
β (°)	79.860(4)	103.952(8)	98.220(6)	115.616(4)
γ (°)	74.600(4)	91.570(9)	95.810(6)	90
$U(\text{\AA}^3)$	10075.7(8)	1735.9(3)	12825(3)	14065.6(14)
Z	1	1	1	8
$\rho_{\rm calc} ({\rm g/cm}^3)$	1.341	1.476	1.331	1.339
$\mu (\mathrm{mm}^{-1})$	0.958	1.358	0.633	1.043
<i>F</i> (000)	4274	796	5404	5904
2θ Range (°)	1.61-27.11	3.82-31.75	1.28-27.15	1.54-26.00
Reflections collected	80497	8788	103909	49858
Unique data	40850	6912	52 591	13840
R _{int}	0.0768	0.0301	0.0855	0.1860
Parameters	1911	433	2278	785
wR_2 (all data)	0.2478	0.1506	0.2391	0.2886
S (Goodness-of-fit)	0.986	1.104	0.909	1.028
$R_1 [I \ge 2\sigma(I)]$	0.0849	0.0410	0.0831	0.0962
Peak, hole $(e \cdot Å^{-3})$	1.1685, -0.744	0.797, -0.952	1.233, -0.641	1.747, -0.771

4. To a solution of 0.10 g (1.00 mmol) 3-hydroxypyridine in 10 mL THF was added 1.00 mmol 'BuLi (0.6 mL, 1.7 M in pentane) and 0.14 g of (1.00 mmol) [CuO^tBu]. After heating the solution to reflux for 1 h a grey precipitate was formed. In a seperate Schlenk tube a solution of 0.28 g (2.00 mmol) [CuO^tBu] in 10 mL THF was added to 0.10 g (1.00 mmol) maleic anhydride. The solution was stirred for 1 h and 0.77 g (2.00 mmol) dppm was added. Combination of both reaction mixtures and heating to reflux for 1 h resulted in a brown solution. Crystals of 4 and a colourless precipitate were obtained by diffusion of pentane into the reaction mixture within a double Schlenk tube. Repeated elemental analysis of the solid residue showed large deviations to calculated values for 4 and indicates the formation of byproducts. The products are insoluble in organic solvents once formed and prevented further characterisation.

2.2. X-ray crystallographic study

Data were measured on a STOE IPDS II (1, 3, 4) and a STOE STADI-4 (2) diffractometer, using Mo K α radiation. The structures were solved by direct methods, and refined by full-matrix least-squares against F^2 using all data (see Table 1 for details) [11]. Organic hydrogen atoms were placed in idealised positions. Non-H atoms were refined with anisotropic thermal parameters; crystals of 1–4 contain large amounts of partially disordered solvent molecules which were refined isotropically. The synthesis of 4 was repeated several times but the dataset presented was the best we were able to obtain.

3. Results and discussion

The acid-base reactions of CuO'Bu with 3-hydroxypyridine (3-pyOH), 2-hydroxypyridine (2-pyOH) and 6-hydroxyquinoline (6-HOQ) in THF at RT produced insoluble grey precipitates. Upon addition of the auxiliary ligand dppm, crystals of 1–3 were obtained from the solutions (Scheme 3).

In the case of $[Cu_{16}(3-pyO)_{16}(dppm)_8]$ (1) (dppm = 1,2bis-diphenylphosphinomethane), NMR and infrared spectra indicated the presence of phosphine ligands and the pyridyl-group but the true nature only became apparent when sensitive single crystals of 1 were analysed by X-ray crystallography (Fig. 1).

In the solid-state, 1 consists of a macrocyclic arrangement of 16 Cu atoms held together by bridging 3-pyO



Scheme 3. Synthesis of 1–3.



Fig. 1. Molecular structure of **1** in the solid-state (phenyl rings of dppm ligands have been omitted; ellipsoids at 50% probability level). Selected ranges of bond lengths (Å) and angles (°): Cu–O 1.990(5)-2.196(5), Cu–N 1.993(6)-2.104(6), Cu–P 2.153(2)-2.188(2), N–Cu–O 97.6(2)-115.7(2), O–Cu–O 83.13(18)-88.34(19), N–Cu–P 107.32(17)-144.22(16), P–Cu–O 102.26(12)-113.33(13) (three-coordinated Cu) 103.4(2)-130.12(19).

and dppm ligands. 32 molecules of THF co-crystallise per macrocycle as lattice solvent; upon the loss of THF, crystals of **1** become amorphous. **1** represents the first Cu(I) complex containing a [3-pyO]⁻ ligand. Two Cu(II) complexes containing 3-pyOH or [3-pyO]⁻ ligands have been reported which also show supramolecular aggregation via hydrogen bonding and sidearm coordination of N atoms



Fig. 2. Molecular structure of **2** in the solid-state (ellipsoids at 50% probability level). Selected bond lengths (Å) and angles (°): Cu(2)–N(1) 1.985(3), Cu(2)–N(2) 1.988(4), Cu(1)–O(2) 1.991(3), Cu(1)–O(1) 2.098(3), Cu(1)–O(1') 2.107(3), Cu(1)–P(1) 2.1472(11), Cu(2)–P(2) 2.1844(11), O(2)–Cu(1)–O(1') 102.59(12), O(2)–Cu(1)–O(1') 96.46(12), O(1)–Cu(1)–O(1') 80.48(11), O(2)–Cu(1)–P(1) 131.75(9), O(1)–Cu(1)–P(1) 119.68(9), O(1')–Cu(1)–P(1) 111.67(8), N(1)–Cu(2)–N(2) 112.30(14), N(1)–Cu(2)–P(2) 127.80(10), N(2)–Cu(2)–P(2) 118.06(11), Cu(1)–O(1)–Cu(1') 99.52(11).

to Cu atoms of adjacent units [12]. The bond distances [Cu–O 1.990(5)–2.196(5) Å, Cu–N 1.993(6)–2.104(6)] in 1 are in the range of commonly observed bond distances in compounds with similar structural motifs [13].

 $[{Cu_2(2-pyO)_2(dppm)}_2]$ (2) was isolated in good yield from the reaction of CuO^tBu and 2-pyOH in the presence of dppm. In the solid-state 2 consists of a centrosymmetric dimer of $[Cu_2(2-pyO)_2(dppm)]$ units. The two Cu atoms in



Fig. 3. Molecular structure in the solid-state of a $[Cu_3(\mu_3-(6-OQ)_2(dppm)_2]^+$ and a $[(6-HOQ)_2(\mu-6-OQ)]^-$ ion present in **3** (ellipsoids at 50% probability level; only α -C atoms of phenyl rings in dppm ligands are displayed). Selected bond lengths (Å) and angles (°): Cu–O 2.147(4)–2.243(4), Cu–P 2.2413(18)–2.2585(19), O(5)···H···O(7) 2.55(1), O(6)···H ···O(7) 2.53(1), O-Cu–O 71.39(17)–73.69(17), O-Cu–P 102.53(13)–122.43(12), P–Cu–P 120.68(7)–122.39(7).

each unit are chelated by two 2-pyO ligands and P atoms of dppm ligands. Whilst Cu(2) is coordinated by two N and P ligand atoms, Cu(1) is four-coordinated by bridging O(1) and O(1'), non-bridging O(2) and P(1) (Fig. 2).

The synthetic route to **1** and **2**, which were both isolated in ca. 70% yield, indicates that reactions of CuO'Bu with arylhydroxides could provide easy access to a variety of Cu(I) aryloxides. The lower pK_a values of arylhydroxides (4–8) in comparison to 'BuOH (ca. 17) favour the onepot-reactions of arylhydroxides with the strong base CuO'Bu over reactions of alkali-metallated aryloxides with Cu(I) halides.

The outcome of the analogous reaction of CuO'Bu with 6-HOQ and dppm is markedly different from the previously described acid–base reactions of arylhydroxides with CuO'Bu. Colourless crystals of $[{Cu_3(\mu_3-6-OQ)_2(dppm)_3} - {(6-HOQ)_2(\mu-6-OQ)}]$ (3) were isolated in 68% yield and the structure was determined by X-ray crystallography (Fig. 3).

In the solid-state, **3** exists as solvent-separated ion-pairs of $[Cu_3(\mu_3-(6-OQ)_2(dppm)_2]^+$ cations and $[(6-HOQ)_2(\mu-6-OQ)]^-$ anions. In the cation three Cu atoms are unsymmetrically bridged by two O atoms of quinolineoxide ligands forming a cage with three dppm ligands. It is the first time that such a structural motif has been observed with Cu(I). Similar cage architectures, however, are known for Cu(II) and mixed-valent complex cations [14,15]. The anion consists of two molecules of 6-HOQ and one [6-OQ]⁻ anion linked by hydrogen bonding. It was impossible to locate H atoms in the Fourier map (all H atoms were added and refined in idealised positions) but direct evidence for



Fig. 4. Solid-state structure of a monomeric unit in **4** (phenyl rings of dppm ligands have been omitted; ellipsoids at 50% probability level). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 2.134(6), Cu(2)–O(2) 1.982(6), Cu(3)–O(5) 1.849(6), Cu(1)–P(1) 2.277(2), Cu(1)–P(3) 2.282(2), Cu(2)–P(2) 2.220(2), Cu(2)–P(4) 2.223(2), Cu(3)–C(50) 1.916(8), O(5)–Cu(3)–C(50) 179.0(3), O(1)–Cu(1)–P(1) 115.21(16), P(1)–Cu(1)–P(3) 128.40(9), O(1)–Cu(1)–P(1) 115.21(16), O(2)–Cu(2)–P(2) 115.92(18), O(2)–Cu(2)–P(4) 119.90(18).



Scheme 4. Synthesis of 4.

undissociated hydroxy protons was found in the infra-red spectrum of **3** ($v_{max} = 3456 \text{ cm}^{-1}$). The 'partial deprotonation approach' used for the synthesis of **3** offers many possibilities for the syntheses of supramolecular assemblies of metal alkoxides stabilised by hydrogen-bonded anions. Current work is focusing on these aspects, and on insertion reactions of organic anhydrides into the metal–oxygen bond of the new Cu(I) alkoxides **1**–**3**. So far these efforts have led to the formation and characterisation of $1/_{\infty}[Cu_3(3-pyO)(CO_2C_2H_4Boc)(dppm^-)(dppm)]_{\infty}$ (**4**) (Boc = tert-butoxycarbonyl) (Scheme 4, Fig. 4).

In the solid-state, **4** exists as a one-dimensional coordination polymer of $[Cu_3(3-pyO)(CO_2C_2H_4Boc)(dppm^{-})-(dppm)]$ -units linked by coordination of N(1) to Cu(1) (Fig. 4). The formation of **4** could be rationalised by co-complexation of [Cu(3-pyO)], $[Cu(CO_2C_2H_4Boc)]$ and $[Cu(dppm^{-})]$ in the presence of an additional auxiliary dppm ligand.

4. Conclusion

The work described here represents a part of our ongoing efforts to establish the 'anhydride-metal alkoxide approach' to metallo-organic open frameworks (MOF's). So far we have successfully described the insertion reactions of a variety of organic anhydrides into the Cu–O bond of the Cu(I) alkoxide [CuO'Bu] and the subsequent metal exchange by metathesis reactions with a variety of transition metal halides. Here we have described the synthesis of a range of novel Cu(I) alkoxides (1–3), which will in future allow the facile construction of polydentate ligands necessary for the formation of MOF's. Future work will focus on these aspects, but the synthesis of 4 illustrates that a number of obstacles are yet to be overcome.

5. Supplementary material

CCDC nos. 285877–285880 contain the supplementary crystallographic data for this paper. These data can be

obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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