SHORT PAPER

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Synthesis and crystal structure of 2,6-bis(imino)phenoxy copper chloride

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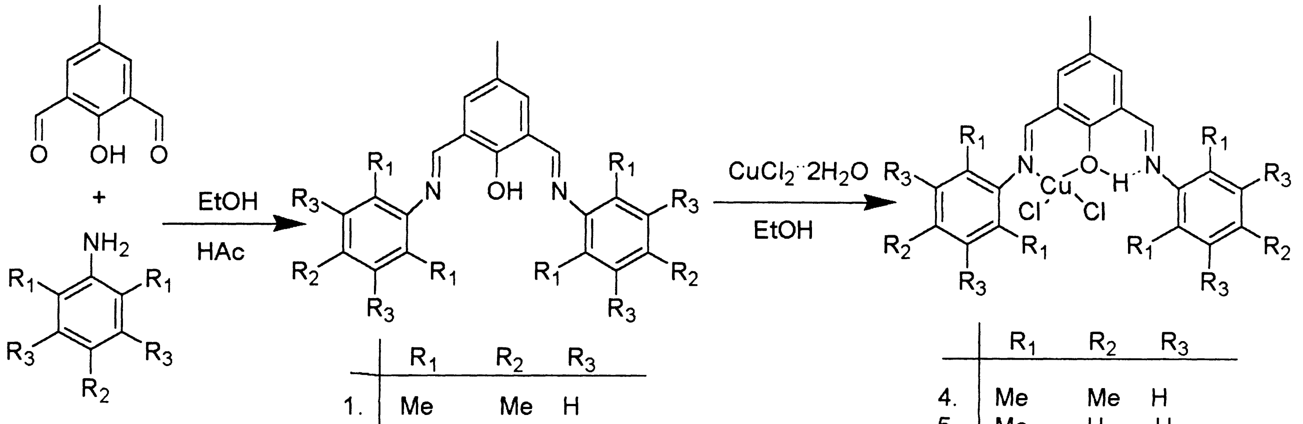
Copper complexes bearing 2,6-bis(imino)phenoxy ligand were synthesised and characterised along with the single crystal X-ray diffraction analysis of complex **4**.

Keywords: crystal, structure, copper(II) complex, 2,6-bis(imino)phenoxy

Driven by industrial application of late transition metal complexes for oligomersation and polymerisation,[1-4] a series of cobalt and nickel complexes bearing 2,6-bis(imino)phenoxy ligands[5] were designed and investigated for oligomerisation. However, it proved difficult to use copper complexes for the oligomerisation and polymerisation.[6] As part of our ongoing investigations regarding the structure and complexation of late-transition metal complexes, herein we describe our studies on the synthesis, characterisation, and the coordinative behaviour of a series of 2,6-bis(imino)phenoxy ligands towards copper (II).

The syntheses of three ligands, 2,6-diformyl-4-methylphenoxybis(2,4,6- trimethylanil) (**1**), 2,6-diformyl-4-methylphenoxybis (2,6-dimethylanil) (**2**) and 2,6-diformyl-4-methyl– phenoxybis(3,5-dimethylanil) (**3**) proceeded through condensation of 2-hydroxy-5-methyl-isophthaldehyde with three substituted anilines by literature methods. Those ligands coordinated with copper chloride to form corresponding complexes (Scheme 1). Elemental analyses of the ligands and complexes agreed well with their calculated data. ^{1}H NMR spectra of the Schiff base ligands showed a single peak about 13.43–14.03 ppm, which was attributed to the presence of the intermolecular hydrogen bond between the phenolic group and the azomethine group at the *cis*-position. Additionally, a group of multiple-signals corresponded to the aromatic protons at about 6.89–7.15 ppm. The infrared spectra of all the three ligands show two very strong absorption bands in the region of 1630–1580 cm^{-1} assigned to the carbon imine stretching mode, supporting the presence of the Schiff-base linkage. In comparison to the Cu (II) complexes, the bands in the region mentioned above undergoes a shift to lower frequency, indicating the coordination of azomethine nitrogen to the copper atom. The mass spectra show reasonable peaks for their *m/z* and fragments (experimental section).

In addition, the single crystal structure of complex **4** was determined by X-ray diffraction analysis. A yellow-brown crystal was grown from a mixture of dichloromethane–hexane (2:1) under slow evaporation. The perspective view of complex **4** is shown in Fig.1 and the selected bond lengths and angles are collected in Table 1. The structure consists of a complex molecule and a CH_2Cl_2 in the crystal. In the complex, the copper atom is four–coordinated by one azomethine nitrogen, one hydroxyl oxygen atom and two chlorides, which forming the distorted tetrahedral coordination sphere around the copper centre. The distances Cu(1)–O(1) 1.927(4) Å, Cu(1)–N(1) 1.968(5) Å, Cu(1)–Cl(1) 2.1877(19) Å, and Cu(1)–Cl(2), 2.2157(19) Å, indicate the interaction of the N, O and Cl with the metal, the Cu(1)–N(1) bond is almost perpendicular to the Cu(1)–O(1) bond, with the O(1)–Cu(1)–N(1) angle at 90.5(2)°. It was found that the



	R1	R2	R3
1.	Me	Me	H
2.	Me	H	H
3	H	H	Me

	R1	R2	R3
4.	Me	Me	H
5	Me	H	H
6	H	H	Me

Scheme 1 Schematic diagram for synthesising ligands and their complexes.

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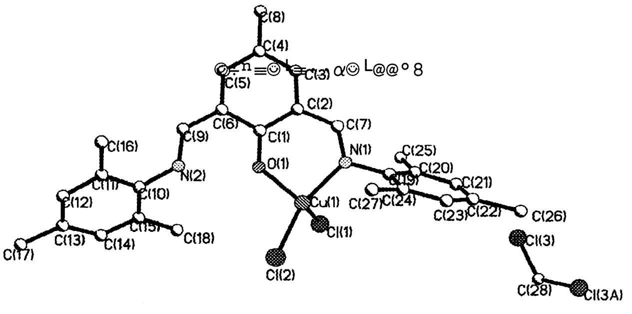

Fig. 1 The molecular structure of complex **4** (hydrogens omitted for clarity).

Table 1 Bond lengths (Å) and angles (°) for complex **4**

Cu(1)–O(1)	1.927(4)	O(1)–Cu(1)–N(1)	90.5(2)
Cu(1)–N(1)	1.968(5)	O(1)–Cu(1)–Cl(1)	133.24(13)
Cu(1)–Cl(1)	2.1877(19)	N(1)–Cu(1)–Cl(1)	102.65(16)
Cu(1)–Cl(2)	2.2157(19)	O(1)–Cu(1)–Cl(2)	97.03(15)
N(1)–C(7)	1.278(6)	N(1)–Cu(1)–Cl(2)	139.89(16)
N(1)–C(19)	1.467(7)	Cl(1)–Cu(1)–Cl(2)	100.40(7)
		C(7)–N(1)–C(19)	116.7(5)
		C(7)–N(1)–Cu(1)	124.0(4)

phenoxy oxygen atom and the one imino nitrogen (*cis*–position) are bound to the metal atom, while another imino nitrogen atom is non–bonding. There exists a strong intermolecular hydrogen bond between the uncoordinated imino-nitrogen atom and the phenoxy-oxygen atom. The hydrogen bond could also be involved with the transformation of two imino-carbon bonds into the *cis*-position in the complex from the *trans*-position of its analogue of the free ligand.[6] The uncoordinated 2, 4, 6-trimethylphenyl ring C(10)–C(11)–C(12)–C(13)–C(14)–C(15) is parallel to the adjacent molecular system C(10A)–C(11A)–C(12A)–C(13A)–C(14A)–C(15A), with a dihedral angle of 0.00°. Therefore there appears to be a weak π–π interaction between molecules due to their centroid distance of 4.256Å. The cell unit is shown in Fig.2.

Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and Cannula techniques. Solvents were refluxed over an appropriate drying agent and distilled under nitrogen prior to use. Using HP-MOD 1106 microanalyzer performed elemental analyses. NMR spectra were recorded on a Bruker spectrometer DMX-300 with TMS as the internal standard. IR spectra were obtained as KBr pellets on a Perkin-Elmer FTIR 2000 spectrometer. Mass spectra were measured on a Kratos AEI MS-50 instrument using either fast atom bombardment (FAB) or electron impact (EI). Melting points were determined with a digital Electrothermal apparatus without further correction. The substituted aniline were purchased from Aldrich Chemical Co.. All other chemicals were obtained commercially and used as received unless stated otherwise.

2,6-Diformyl-4-methylphenoxybis(2,4,6-trimethylanil) (**1**): 2-Hydroxy-5-methyliso phthaldehyde (1.3g, 7.97mmol) and 2,4,6-dimethylaniline (2.2g, 16.5mmol) were magnetically stirred in anhydrous ethanol (15 ml) under N_2 at 50°C for 2h, after which the colour of the solution was yellow. The reaction mixture was cooled to room temperature, the solvent volume was removed under reduced pressure, and then left in a refrigerator overnight. The yellow product was filtered and crystallised from ethanol, yield 1.53g (73%). M.p.: 155–156 °C, IR (KBr pellet) ν/cm^{-1}: 3444 (br, -OH), 2917 (s),1630 (vs, HC=N),1593 (m, HC=N), 1478 (s), 1462 (s), 855. ^{1}H NMR (400MHz, $CDCl_3$), δ 13.57 (1H, Ar–O*H*), 8.52 (br, 2H, *H*C=N), 6.89 (m, 6H, Ar–*H*), 2.38 (s, 3H, Ar–C*H*$_3$), 2.27 (s, 6H, Ar–C*H*$_3$), 2.15 (12H, Ar–C*H*$_3$), 1.63 (s, 3H, Ar–C*H*$_3$). MS (EI): *m/z* (%) 398 (M$^+$ 9.9), 279 (6.4), 265 (18.9), 264(84.2), 146 (10.0), 135 (12.8), 134 (8.2), 119 (7.1). Anal. calc. for $C_{27}H_{30}ON_2$ (398): C, 81.37; H, 7.59; N, 7.03. Found C, 81.24; H, 7.68; N, 6.87.

2,6-Diformyl-4-methylphenoxybis(2,6-dimethylanil) (**2**): Ligand **2** was similarly prepared as described for ligand **1** using 2-hydroxy-5-methyl-isophthaldehyde with 2,5-dimethylaniline as a yellow powder in 71.4% yield. M.p.136–137°C. IR (KBr) *ν*/cm^{-1}: 3446 (br, m, -OH), 2919 (m), 1630 (vs, C=N), 1588 (vs, C=N), 1468 (vs), 1311 (m), 1194, 1091, 1036, 980, 768, 619, 556. ^{1}H NMR ($CDCl_3$) δ: 13.52(s, 1H, Ar–O*H*), 8.32-8.60 (br, 2H, *H*C=N), 7.28(s, 2H, Ar–H), 7.15 (s,

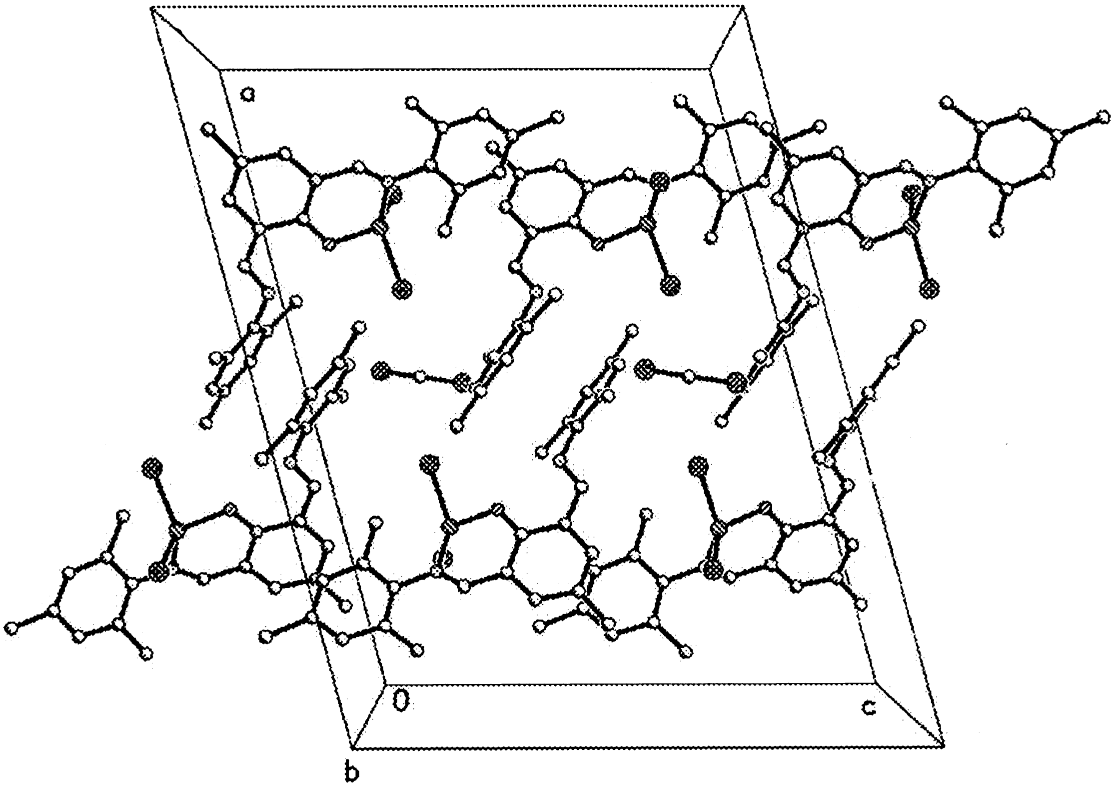

Fig. 2 The cell unit of complex **4**

4H, Ar–*H*), 7.06(s, 2H, Ar–H), 2.46(s, 3H, Ar–C*H*$_3$), 2.25 (s, 12H, Ar–C*H*$_3$). EI-MS (*m/z*, %) 370 (M$^+$, 5.4), 265 (7.5), 251 (15.0), 250 (83.2). Anal. calc. for $C_{25}H_{26}N_2O$: C, 81.08; H, 7.03; N, 7.56. Found: C, 80.79; H, 6.98; N, 7.48.

2,6-Diformyl-4-methylphenoxybis(3,5-dimethylanil) (**3**): Ligand **3** was similarly prepared as described for ligand **1** using 2-hydroxy-5-methyl-isophthaldehyde with 3,5-dimethylaniline as a red powder in 97% yield. M.p.161–162°C. IR (KBr pellet, ν/cm^{-1}) 3441 (br, -OH), 2917 (s), 1607 (vs, HC=N), 1580 (vs, HC=N), 1459 (s), 844, 687. ^{1}H NMR ($CDCl_3$) δ: 14.03 (s, 1H, Ar-O*H*), 8.83 (br, 2H, *H*C=N), 6.92 (m, 8H, Ar-*H*), 2.37 (s, 12H, Ar-C*H*$_3$), 1.25 (s, 3H, -C*H*$_3$); EI–MS *m/z* 370 (M$^+$, 89.9), 369(M$^+$–1, 24.4), 355 (6.7), 353 (6.3), 266 (22.8), 265 (100), 251 (12.2); Anal. calc. for $C_{25}H_{26}N_2O$: C, 81.05; H, 7.07; N, 7.56. Found: C, 81.10; H, 7.11; N, 7.48.

{2,6-Diformyl-4-methylphenoxybis(2,4,6-trimethylanil)}CuCl$_2$ **(4):** $CuCl_2 \cdot 2H_2O$ (21.0mg 0.12mmol) and ligand **1** (50mg, 0.13mmol) were stirred at 50°C in absolute ethanol (15 ml). After 2 h, the mixture was cooled to room temperature, and diethyl ether (5ml) was added to precipitate the product as yellow-brown power, which was washed with ether and vacuum dried, yield 41.1mg (60%). IR (KBr pellet) ν/cm^{-1}: 3466, 2918, 1629, 1544, 1480, 1199, 1078, 556. MS (FAB): 496 (M$^+$-Cl), 461 (M$^+$-2Cl), 398 (L). Anal. calc. for $C_{27}H_{30}N_2OCuCl_2 \cdot 1/2H_2O$. C, 58.80; H, 5.44; N, 5.08. Found: C, 59.73; H, 5.96; N 4.78.

{2,6-Diformyl-4-methylphenoxybis(2,6-dimethylanil)}CuCl$_2$ **(5):** Prepared in the similar way as described in complex **4**, using ligand **2** and $CuCl_2 \cdot 2H_2O$, complex **5** was obtained in 33.3% yield. IR (KBr pellet) ν/cm^{-1}: 3453, 2923, 1634(s), 1545(s), 1475, 1330, 1290, 1182, 997, 880, 775, 506. FAB (MS): 433 (L+Cu), 371(L). Anal calc for $C_{25}H_{26}ON_2CuCl_2 \cdot 1/2H_2O$. C, 57.36; H, 5.0; N, 5.4; Found: C, 57.25; H, 5.2; N, 4.8.

{2,6-Diformyl-4-methylphenoxybis(3,5-dimethylanil)}CuCl$_2$ **(6):** Prepared in the similar way as described in complex **4**, using ligand **3** and $CuCl_2 \cdot 2H_2O$, complex **6** was obtained in 63.75% yield. IR (KBr pellet) ν/cm^{-1}: 3453, 2918, 1638(s), 1588(s), 1542, 1380, 1232, 1034, 823, 687, 530. MS (FAB): 865 (2M$^+$-$CuCl_2$), 433 (L+Cu), 371(L+1). Anal calc for $C_{25}H_{26}ON_2CuCl_2 \cdot H_2O$. C, 57.36; H, 5.0; N, 5.4. Found: C, 57.62; H, 4.9; N, 5.0.

Crystallographic data for **4**: $C_{27.50}$ H_{31} C_{l3} Cu N_2 O, M=575.43, crystal size: 0.59 x 0.47 x 0.27 mm, Monoclinic, C2/c, *a* = 22.293(2) Å, *b*=14.8101(13) Å, *c*=17.2893(13) Å, β=105.389(3), *Z*=8, V=5503.6(8) Å^3, Dc=1.389 Mg/m^3, F (000)=2384, R1 = 0.0548, wR2 = 0.0565. Structure analyses for copper complex was performed on a Bruker SMART diffractometer at 298(2) K with graphite-monochromated Mo K_α (λ= 0.71073Å) by ω–2θ scan technique in the range 2.21 – 27.48 °. A total of 12132 reflections were collected, 6303 reflection with [$I > 2\sigma(I)$] were used in the structure determination and refinement. The structure was solved by direct methods using the SHELXTL-97 package. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located theoretically and refined with riding mode position parameters and fixed isotropic thermal parameters. The crystallographic data were deposited with the Cambridge Crystaallographic Data Centre (CCDC-189844).

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