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FULL PAPER

Synthesis, magnetism, ^{1}H NMR and redox activity of dicopper(II) complexes having a discrete $\{Cu_2(\mu\text{-phenoxide})_2\}^{2+}$ unit supported by a non-macrocyclic ligand environment. Crystal structure of $[Cu_2(L)_2(OClO_3)_2]$ [HL = 4-methyl-2,6-bis(pyrazol-1-ylmethyl)-phenol] †

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Received 6th September 1999, Accepted 16th September 1999

Reaction between 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol (HL) or its 3,5-dimethylpyrazole derivative (HL′) and $Cu(ClO_4)_2\cdot 6H_2O$ afforded $[Cu^{II}_2(L/L')_2(OClO_3)_2]$ **1** and **2**. Complex **1** has been structurally characterized showing that each copper(II) centre is square pyramidal with two bridging phenoxide oxygens and two terminal pyrazole nitrogens in the equatorial plane and a perchlorate oxygen atom axially co-ordinated. Variable-temperature magnetic susceptibility measurements revealed that the dicopper(II) centres are strongly antiferromagnetically coupled [singlet–triplet energy separation, $2J$ (in cm^{-1}): −1204 for **1** and −798 for **2**]. The complexes exhibit ^{1}H NMR spectra within δ 0–10 due to their $S = 0$ ground state. In MeCN solution they exhibit ligand field transitions in the range 14 300–16 600 cm^{-1} and phenolate-to-copper(II) charge-transfer transition at ≈22 700 cm^{-1}. In MeCN solution each complex displays three consecutive irreversible responses (scan rate of 50 mV s^{-1}) with E_{pc} values (V *vs.* SCE) at −0.02, −0.54 and −0.86 (**1**) and 0.00, −0.42 and −0.80 (**2**). The first two responses are due to Cu^{II}–Cu^{I} and the most cathodic response to Cu^{I}–Cu^{0} redox processes, respectively.

Introduction

Dicopper(II) complexes with endogenous bridging phenolate ligands are of ongoing interest [1–3] because of their relevance to copper-containing enzymes, tyrosinase [4] and catechol oxidase,[5] and/or due to their interesting magnetic properties. This work stems from our continued activity [6] on chemical modelling of tyrosinase using tailor-made binucleating non-Schiff base ligands, capable of providing only two nitrogen co-ordination to each copper centre. During investigation on the reactivity of a μ-peroxo-bridged copper(II) complex of tris(3,5-dimethylpyrazolyl)hydridoborate with externally added phenolic substrate 2,6-dimethylphenol, Kitajima *et al.*[7] proposed a diphenoxo-bridged copper(II) intermediate. As the active site of tyrosinase is quite open,[4b,c] we felt that synthesis and structural characterisation of diphenoxo-bridged copper(II) complexes with only two pyrazole co-ordination at the terminals would be a valuable complement to Kitajima's work. We report here the synthesis and characterisation of two di-μ-phenoxo-bridged copper(II) complexes with HL [4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol] and its 3,5-dimethylpyrazole derivative HL′, $[Cu^{II}_2(L/L')_2(OClO_3)_2]$ **1** and **2**. Temperature-dependent magnetic studies on solid samples of **1** and **2** provide a systematic comparison of magneto-structural aspects of diphenoxo-bridged copper(II) complexes. The complexes belong to a relatively new family of structurally characterised copper(II) complexes having a $\{Cu^{II}_2(\mu\text{-phenoxide})_2\}^{2+}$ motif in a non-macrocyclic/non-Schiff base nitrogen-donor ligand environment.[8–11]

Experimental

Reagents and materials

All chemicals were obtained from commercial sources and used as received. Solvents were dried as reported previously.[6,12] *n*-Hexane was dried by refluxing over Na. Copper(II) perchlorate hexahydrate was prepared from copper(II) carbonate and aqueous (1 : 1 v/v) $HClO_4$. Tetra-*n*-butylammonium perchlorate was prepared/purified as before.[12a]

Syntheses

4-Methyl-2,6-bis(pyrazol-1-ylmethyl)phenol, HL. The methodology followed to prepare this ligand (which does not require any chromatographic purification such as that reported [13]) is adapted from Sorrell *et al.*[14]

2,6-Bis(hydroxymethyl)-4-methylphenol. The method described below has been adapted from Drago *et al.*[15] 4-Methylphenol (15 g, 0.139 mol) was added to an aqueous 5% NaOH solution (120 cm^3) and the mixture stirred with gentle heating (≈40 °C) to dissolve the starting material. The solution was then cooled to ≈25 °C and 37% HCHO solution (23 cm^3) added and stirred for 6 d at room temperature. Upon addition of concentrated HCl (12 cm^3) a yellow solid resulted which was filtered off, washed thoroughly with water and air-dried (22 g, 94%). Found: C, 64.14; H, 7.10. Calc. for C_3H_4O: C, 64.29; H, 7.14%. ^{1}H NMR (60 MHz, $CDCl_3$, 298 K): δ 6.80 (2 H, s, aromatic protons), 4.55 (4 H, s, CH_2OH) and 2.05 (3 H, s, CH_3).

4-(Benzyloxy)-2,6-bis(hydroxymethyl)toluene. Sodium metal (1.5 g, 0.065 mol) was dissolved in dry EtOH (300 cm^3). To this was added 2,6-bis(hydroxymethyl)-4-methylphenol (11 g, 0.065 mol), followed by benzyl chloride (8.4 g, 0.066 mol) and sodium iodide (2 g, 0.013 mol). The resulting mixture was then refluxed for 7 h. The above cooled mixture was poured into a beaker filled with crushed ice and the solution made sufficiently alkaline by strong NaOH solution. It was left overnight to settle the curdy precipitate, which was filtered off, washed thoroughly with water and air-dried (12 g, 72%). Found: C, 74.51; H, 6.92. Calc. for $C_{16}H_{18}O_3$: C, 74.42; H, 6.98%. GC mass spectrum: *m*/*z* 258 (65%); calc. for $C_{16}H_{18}O_3$ 258. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.46–7.35 (5 H, m, aromatic protons of PhCH_2O),

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4025/

7.16 (2 H, s, aromatic 4/6H of *m*-xylyl ring), 4.95 (2 H, s, PhCH_2O), 4.68 (4 H, s, CH_2OH) and 2.33 (3 H, s, CH_3).

4-(Benzyloxy)-2,6-bis(chloromethyl)toluene. To a solution of 4-(benzyloxy)-2,6-bis(hydroxymethyl)toluene (5 g, 0.019 mol) in CH_2Cl_2 (100 cm^3), was added dropwise $SOCl_2$ (17 g, 0.014 mol). After stirring for 3 h the solution was evaporated to dryness under a gentle stream of dinitrogen. After addition of CH_2Cl_2 (50 cm^3) the solution was again evaporated to dryness (5.66 g, 98%). Found: C, 65.14; H, 5.40. Calc. for $C_{16}H_{16}Cl_2O$: C, 65.09; H, 5.42%. GC mass spectrum: *m*/*z* 294 (30%); calc. for $C_{16}H_{16}Cl_2O$ − H 294. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.52–7.34 (5 H, m, aromatic protons of PhCH_2O), 7.23 (2 H, s, aromatic 4/6 H of *m*-xylyl ring), 5.08 (2 H, s, PhCH_2O), 4.62 (4 H, s, CH_2Cl) and 2.34 (3 H, s, CH_3).

4-(Benzyloxy)-2,6-bis(pyrazol-1-ylmethyl)toluene. Sodium hydride (1.73 g, 0.072 mol) was suspended in dmf (40 cm^3) and pyrazole (1.844 g, 0.27 mol) added, under a dry dinitrogen atmosphere. The mixture was then stirred for 1 h. To this was added dropwise 4-(benzyloxy)-2,6-bis(chloromethyl)toluene (4 g, 0.14 mol) in dmf (25 cm^3). The resulting mixture was magnetically stirred for 4 d at ≈25 °C. Addition of water (15 cm^3) followed by solvent evaporation under reduced pressure afforded a slurry, to which was added an aqueous 10% NaOH solution (25 cm^3). The protected ligand was extracted with CH_2Cl_2 (40 cm^3) and the organic layer washed with water, followed by drying over anhydrous Na_2SO_4. Solvent removal to one-third under reduced pressure afforded a yellow oil, to which *n*-hexane (15 cm^3) was added to give a brownish white product (3.51 g, 72%). Found: C, 73.82; H, 6.20; N, 15.71. Calc. for $C_{22}H_{22}N_4O$: C, 73.74; H, 6.15; N, 15.64%. GC mass spectrum: *m*/*z* 355 (25%); calc. for $C_{22}H_{22}N_4O$ − 3H 355. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.54–7.26 (7 H, m, aromatic protons of PhCH_2O and 3/5-pyrazole protons), 6.81 (2 H, s, 4/6-protons of *m*-xylyl ring), 6.26 (2 H, t, pyrazole 4-H proton), 5.32 (4 H, s, C$H_2N_2C_3H_3$), 4.76 (2 H, s, OCH_2Ph) and 2.20 (3 H, s, CH_3).

HL. 4-(Benzyloxy)-2,6-bis(pyrazol-1-ylmethyl)toluene (3.51 g, 9.8 mmol) was refluxed with concentrated HBr (40 cm^3) and water (56 cm^3) for 10 h. The reaction mixture was then cooled to room temperature and neutralised to pH 7 with aqueous NaOH solution (10 mol dm^{-3}). The HL was then extracted with CH_2Cl_2 (40 cm^3) and the organic layer dried over anhydrous Na_2SO_4. The organic extract was then concentrated to one-fifth of its initial volume and addition of *n*-hexane (≈15 cm^3) resulted in precipitation of a white solid. It was filtered off, washed with *n*-hexane and air-dried (2.8 g, 94%). Found: C, 67.14; H, 6.12; N, 21.10. Calc. for $C_{15}H_{16}N_4O$: C, 67.16; H, 5.97; N, 20.90%. GC mass spectrum: *m*/*z* 268 (55%); calc. for $C_{15}H_{16}N_4O$ 268. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.53–7.49 (4 H, m, pyrazole 3/5 protons), 6.92 (2 H, s, aromatic protons of *m*-xylyl ring), 6.25 (2 H, t, pyrazole 4-H), 5.27 (4 H, s, $CH_2N_2C_3H_3$) and 2.20 (3 H, s, CH_3).[13]

2,6-Bis(3,5-dimethylpyrazol-1-ylmethyl)-4-methylphenol, HL′. The method used to prepare this new ligand was as described above except for 3,5-dimethylpyrazole in place of pyrazole. The coupling reaction and final deprotection step are described below.

4-(Benzyloxy)-2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)-toluene. Sodium hydride (0.73 g, 0.031 mol) was suspended in dmf (20 cm^3) and 3,5-dimethylpyrazole (1.11 g, 0.115 mol) added, under a dry dinitrogen atmosphere. The mixture was then stirred for 1 h. To this was added dropwise 4-(benzyloxy)-2,6-bis(chloromethyl)toluene (1.7 g, 0.058 mol) in dmf (10 cm^3). The resulting mixture was magnetically stirred for 4 d at ≈25 °C. Addition of water (10 cm^3) followed by solvent evaporation under reduced pressure afforded a slurry, to which was added an aqueous 10% NaOH solution (15 cm^3). The protected ligand was extracted with CH_2Cl_2 (30 cm^3) and the organic layer washed with water, followed by drying over anhydrous Na_2SO_4. Solvent removal to one-third of its original volume, under reduced pressure, afforded a yellow oil, to which *n*-hexane (≈20 cm^3) was added to give a brownish white product (2.3 g, 96%). Found: C, 75.40; H, 7.30; N, 13.43. Calc. for $C_{26}H_{30}N_4O$: C, 75.36; H, 7.25; N, 13.53%. GC mass spectrum: *m*/*z* 415 (6%); calc. for $C_{26}H_{30}N_4O$ + H 415. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.43 (5 H, s, aromatic protons), 6.38 (2 H, s, aromatic protons), 5.84 (2 H, s, pyrazole 4-H protons), 5.21 (4 H, s, C$H_2N_2C_3HMe_2$), 4.71 (2 H, s, OCH_2Ph), 2.25 (6 H, s, CH_3), 2.14 (3 H, s, CH_3) and 2.06 (6 H, s, CH_3).

HL′. 4-(Benzyloxy)-2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)-toluene (2.3 g, 5.6 mmol) was refluxed with concentrated HBr (25 cm^3) and water (38 cm^3) for 10 h. The reaction mixture was then cooled to room temperature and neutralised to pH 7 with an aqueous NaOH solution (10 mol dm^{-3}). The HL′ was then extracted with CH_2Cl_2 (30 cm^3) and the organic layer dried over anhydrous Na_2SO_4. The organic extract was concentrated to one-fifth of its initial volume and addition of *n*-hexane (≈10 cm^3) resulted in precipitation of a white solid. It was filtered off, washed with *n*-hexane and air-dried (1.7 g, 92%). Found: C, 70.40; H, 7.51; N, 17.32. Calc. for $C_{19}H_{24}N_4O$: C, 70.37; H, 7.41; N, 17.28%. GC mass spectrum: *m*/*z* 327 (4%); calc. for $C_{19}H_{24}N_4O$ + 3H 327. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.70 (2 H, s, aromatic protons), 5.82 (2 H, s, pyrazole 4-H protons), 5.15 (4 H, s, C$H_2N_2C_3HMe_2$), 2.24 (6 H, s, CH_3), 2.22 (6 H, s, CH_3) and 2.07 (3 H, s, CH_3).

$[Cu_2(L)_2(OClO_3)_2]$ 1. To a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.138 g, 0.38 mmol) in MeOH (5 cm^3) was added dropwise a mixture of HL (0.1 g, 0.38 mmol) and triethylamine (0.04 g, 0.38 mmol) in MeOH (6 cm^3), under magnetic stirring. The resulting reddish brown mixture was further stirred for 2 h at 298 K. The brown precipitate thus formed was collected by filtration, washed with MeOH and vacuum dried. Recrystallisation from MeCN–$MeCO_2Et$ (vapour diffusion) afforded a crystalline solid suitable for structural studies. Yield = 62%. Found: C, 42.18; H, 3.53; N, 13.19. Calc. for $C_{15}H_{15}ClCuN_4O_5$: C, 41.90; H, 3.52; N, 13.03%. IR (KBr disc, selected peaks): 1110, 1070, 1055, 630 and 620 cm^{-1} ($\nu(ClO_4)$). Conductivity (MeCN, ≈10^{-3} mol dm^{-3} solution at 298 K): Λ_M = 225 Ω^{-1} cm^2 mol^{-1}. UV/VIS, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): (MeCN) 668 (665), 441 (6330), 328 (sh) (3050) and 282 (11 100); (Nujol mull) 1050–650 (very broad feature) and 480. ^{1}H NMR (CD_3CN): δ 2.11, 3.14, ≈6.00 (vbr), 7.39 (shoulder on right), 7.65 and 9.86.

$[Cu_2(L')_2(OClO_3)_2]$ 2. A similar procedure on the same scale as that described for complex **1** was followed. To a magnetically stirred solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.114 g, 0.31 mmol) in MeOH (6 cm^3) was added dropwise a mixture of HL′ (0.1 g, 0.31 mmol) and triethylamine (0.032 g, 0.31 mmol) in MeOH (8 cm^3). The reddish brown mixture formed was further stirred for 2 h at 298 K. It was then concentrated to one-third of its initial volume, diethyl ether (4 cm^3) added and kept in a deep freeze. After 2 h a brownish green crystalline material precipitated and was collected by filtration, washed with diethyl ether and dried *in vacuo*. Yield = 73%. Found: C, 46.51; H, 4.60; N, 11.40. Calc. for $C_{19}H_{23}ClCuN_4O_5$: C, 46.90; H, 4.70; N, 11.50%. IR (KBr disc, selected peaks): 1120, 1090, 1065, 630 and 625 cm^{-1} ($\nu(ClO_4)$). Conductivity (CH_3CN, 10^{-3} mol dm^{-3} solution at 298 K): Λ_M = 232 Ω^{-1} cm^2 mol^{-1}. Absorption spectrum [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): (in MeCN) 620 (900), 438 (5020), 330 (sh) (2740) and 280 (10 450)]; (Nujol mull) 990 (sh), 700 and 460. ^{1}H NMR (CD_3CN): δ 1.36, 2.51, 2.69, 5.02, 7.00, 7.39 and 7.88.

CAUTION: perchlorate salts of compounds containing organic ligands are potentially explosive!

Physical measurements

Elemental analyses were obtained from either Indian Associ-

ation for the Cultivation of Science, Calcutta or National Chemical Laboratory, Pune. Solution electrical conductivity measurements were carried out with an Elico (Hyderabad, India) Type CM-82 T conductivity bridge. Spectroscopic data were obtained by using the following instruments: infrared, Perkin-Elmer M-1320; electronic, Perkin-Elmer Lambda 2; ^{1}H NMR, PMX-60 JEOL (60 MHz) or JEOL-JNM-LA-400 FT (400 MHz) NMR spectrometer; GC MS spectra (in $CHCl_3$ solution), GC 8000^{TOP} spectrometer (Finnigan, UK).

Magnetism

Variable-temperature solid-state magnetic susceptibility measurements were done by the Faraday technique using a local built magnetometer.[12b,c] All measurements were made at a fixed main field strength of ≈10 kG. Susceptibilities were corrected for diamagnetic contribution, by using literature tabulations.[16]

Cyclic voltammetry

Cyclic voltammetric measurements were performed by using a PAR model 370 electrochemistry system.[12a] A platinum-inlay (Beckman) electrode was used as the working electrode. All potentials were measured with reference to the saturated calomel electrode (SCE) at 298 K; no corrections were made for junction potentials.

Crystallography

A brown crystal of complex **1** was used for intensity data collection (θ–2θ scan technique) using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD-4 Mach diffractometer. Lattice parameters were obtained from least-squares analyses of 25 machine-centred reflections. Data were corrected for Lorentz-polarisation effects; analytical absorption corrections were also applied. Anomalous dispersion was applied for all non-hydrogen atoms. All calculations were performed using the XTAL 3.2 program package.[17] The structure was solved by direct methods and successive Fourier-difference syntheses. All refinements were performed by full-matrix least squares on *F*. The positions of the hydrogen atoms were calculated assuming ideal geometries, but not refined. All other atoms were refined with anisotropic thermal parameters.

Crystal data. $C_{30}H_{30}Cl_2Cu_2N_8O_{10}$, $M = 860$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.085(8)$, $b = 10.249(5)$, $c = 10.472(1)$ Å, $\alpha = 96.55(2)$, $\beta = 110.17(2)$, $\gamma = 115.77(2)°$, $U = 869.3(0.6)$ Å^3; $T = 293$ K, $Z = 1$, μ(Mo-Kα) = 1.45 mm^{-1}, 3336 reflections measured, 3056 unique which were used in all calculations. The final $wR(F)$ was 0.051, $R1 = 0.043$.

CCDC reference number 186/1659.

See http://www.rsc.org/suppdata/dt/1999/4025/ for crystallographic files in .cif format.

Results and discussion

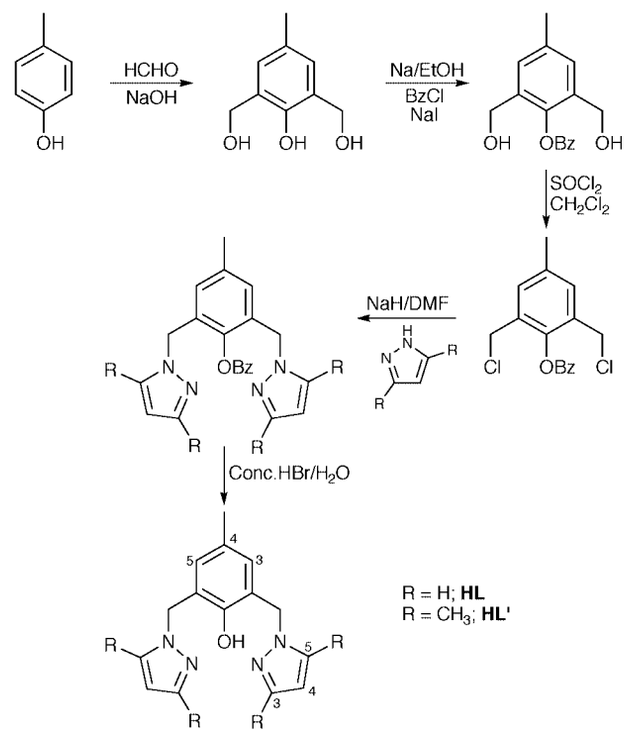
Syntheses

The ligands 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol (HL) and its 3,5-dimethylpyrazole derivative (HL′) have been prepared from 4-methylphenol as starting material and Scheme 1 illustrates the steps involved. It should be emphasised here that HL′ is new and the syntheses of HL and HL′ do not require any chromatographic manipulation.

Stirring methanolic solutions of the deprotonated form of HL or HL′ with copper(II) perchlorate hexahydrate afforded isolation of two brown to brownish green crystalline solids of composition, $[Cu_2(L/L')_2(OClO_3)_2]$ **1** and **2**. The IR spectra clearly demonstrated[18] the presence of co-ordinated perchlorate ions; however in MeCN solution they are dissociated (solution electrical conductivity data, 1 : 2 electrolyte).[19]

Table 1 Selected bond lengths (Å) and angles (°) for $[Cu_2(L)_2(OClO_3)_2]$ **1**

Cu–N(2)	1.996(7)	Cu–O(1a)	1.971(5)
Cu–N(3)	1.985(4)	Cu–O(1a′)	1.952(3)
Cu···Cu′	3.0983(8)	Cu–O(2)	2.408(6)
O(2)–Cu–N(2)	91.6(2)	N(2)–Cu–N(3)	91.0(2)
O(2)–Cu–N(3)	84.1(2)	N(2)–Cu–O(1a)	165.0(3)
O(2)–Cu–O(1a)	102.9(2)	N(2)–Cu–O(1a′)	97.8(2)
N(3)–Cu–O(1a)	94.1(2)	N(3)–Cu–O(1a′)	168.7(2)
O(1a)–Cu–O(1a′)	75.6(2)		



Scheme 1 Bz = Benzyl.

Crystal structure of $[Cu_2(L)_2(OClO_3)_2]$ 1

In order to determine unambiguously the structure of complexes **1** and **2** a single-crystal structure determination on **1** was undertaken. Given in Fig. 1 is a view of the molecule. Selected bond distances and angles are listed in Table 1. The molecule sits on a crystallographically imposed centre of inversion, forming the bridged dinuclear structure with each copper being five-co-ordinate. The co-ordination in the basal plane at each copper(II) centre is provided by two bridging phenoxide oxygen atoms and two terminal pyrazole nitrogen atoms, from two anionic L ligands. The perchlorate ions are transaxially bound above and below the dinuclear centres. The copper centres are displaced toward the perchlorate oxygen atoms by 0.255 Å from the mean N_2O_2 basal plane. Based on the Addison structural distortion index parameter ($\tau = 0.06$),[20] the co-ordination environment around each Cu atom is almost perfect square pyramidal. The sum of the angles at the phenoxide oxygens is almost exactly 360° (O(1a) 359.8°), indicating no pyramidal oxygen distortion. An interesting structural feature is the dihedral angle between the planes of the phenoxide ring and the Cu_2O_2 bridge, which is ≈55°.

The average terminal Cu–N (pyrazole) distance (1.991 Å) is comparable to that reported,[21] and the average bridging Cu–O (phenoxide) bond distance (1.962 Å) is similar to those of reported diphenoxo-bridged complexes.[8a,9b,11,22a] The Cu–O (perchlorate) bond length of 2.408(6) Å is comparable [2.394(3) Å] to that in a closely related structure[23a] in a macrocyclic environment; however, it is shorter than that recently reported

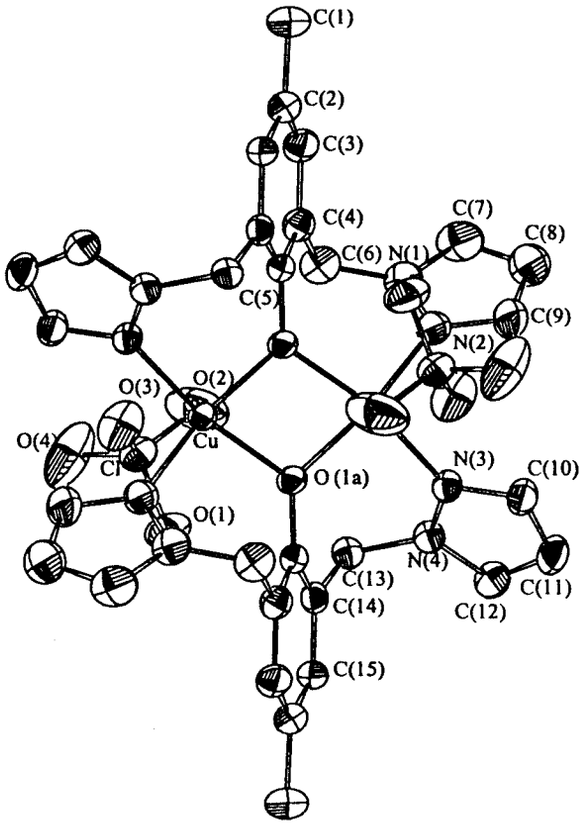


Fig. 1 View of the molecular structure of $[Cu_2(L)_2(OClO_3)_2]$ **1**. Hydrogen atoms are omitted for clarity. Unlabelled atoms are related to labelled atoms by the crystallographic centre of inversion.

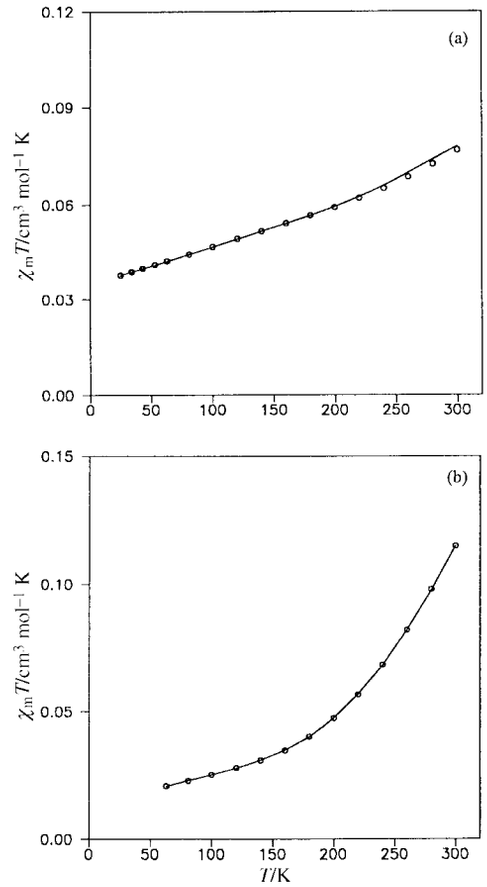


Fig. 2 Plot of $\chi_m T$ (per dimer) *versus* temperature for polycrystalline samples of (*a*) $[Cu_2(L)_2(OClO_3)_2]$ **1** and (*b*) $[Cu_2(L')_2(OClO_3)_2]$ **2**.

for a diphenoxo-bridged dicarbaldehyde complex [2.504(5) Å].[22a] The other bond distances and angles are not exceptional. The Cu–O–Cu′ angle of 104.4(2)° is very much to the higher end of the values observed for diphenoxo-bridged copper(II) complexes of macrocyclic[23b] as well as non-macrocyclic ligands.[8a,9a,10b–d] The observed Cu · · · Cu separation 3.0983(8) Å falls in the range (2.901–3.345 Å) reported for diphenoxo-bridged copper(II) complexes of macrocyclic[23] as well as non-macrocyclic ligands.[8b,9b,10c,d]

Magnetism

In order to extract information about the nature and extent of magnetic exchange interaction between the two copper(II) centres, temperature-dependent magnetic susceptibility measurements on powder samples of **1** and **2** were carried out. The magnetic behaviour (Fig. 2) is typical of very strong antiferromagnetic coupling between pairs of copper(II) centres. The μ_{eff} per Cu (300 K) values are 0.55 μ_B for **1** and 0.68 μ_B for **2**. The experimentally observed χ_m values (per dimer) may be expressed using the modified Bleaney–Bowers expression (1),

$$\chi_m = \frac{2N\beta^2g^2}{kT}[3 + \exp(-2J/kT)]^{-1}(1 - \rho) + \frac{N\beta^2g^2}{2kT}\rho + 2N_\alpha \quad (1)$$

which includes a very small corrective term, ρ, for non-coupled copper(II) impurity and N_α is the temperature-independent paramagnetism (t.i.p.).[6b] The singlet–triplet energy gap is expressed in terms of $2J$ and other symbols have their usual meanings. Keeping t.i.p. and g fixed at 60×10^{-6} cm^3 mol^{-1} and 2.00 respectively, the J and ρ parameters were determined by minimising $R = \Sigma(\chi_m^{obs} - \chi_m^{calc})^2/\Sigma(\chi_m^{obs})^2$. Non-linear regression analysis of the data using eqn. (1) gave good data fits: $J = -602$ cm^{-1}, $\rho = 0.042$ and $R = 3.011 \times 10^{-10}$ for **1**; $J = -399$ cm^{-1}, $\rho = 0.016$ and $R = 8.74 \times 10^{-11}$ for **2**. Given the large experimental uncertainties for almost diamagnetic compounds (particularly for **1**) the calculated J values are far too accurate. However, the analyses correspond to excellent agreement between observed and calculated magnetic data (Fig. 2). The Cu_2O_2 plane is expected to be non-planar in **2**, which would result in reduced magnetic exchange coupling.

The increased value of the Cu–O–Cu′ bridge angle (104.4°) observed in complex **1** implies greater s character in the bridging orbitals which in turn produces increased antiferromagnetic coupling. This is in line with theoretical predictions.[24] The non-planarity of the planes of the phenoxide ring and Cu_2O_2 bridge unit (*cf.* crystal structure) is expected to have consequences for the observed magnetic behaviour of **1** and **2**, since the O atom orbitals involved in transmitting superexchange between the copper ions will be affected. Given the results at hand we are not in a position to throw more light on the mechanism of spin exchange in these compounds.

From the standpoint of magneto-structural correlation, the observed Cu–O–Cu′ angle and the $2J$ value of complex **1** follow the trend on the linear plot provided by Thompson *et al.*[23b] for macrocyclic systems.

Spectral properties

The brown complexes **1** and **2** exhibit in CH_3CN solution strong ligand-to-metal charge-transfer (LMCT) transitions at ≈22 700 cm^{-1}. Much weaker absorption is also found in the region 14 300–16 600 cm^{-1}, associated with d–d transitions of a square-based copper(II) centre.[25]

In line with their magnetic behaviour, complexes **1** and **2** are EPR silent. In CD_3CN solution (298 K) they exhibit reasonably sharp well resolved ^{1}H NMR signals over a relatively small range δ 0–12 (Fig. 3). The remarkably simple spectra are due to their symmetric structure in solution. A tentative assignment of the resonances could be made through consideration of relative

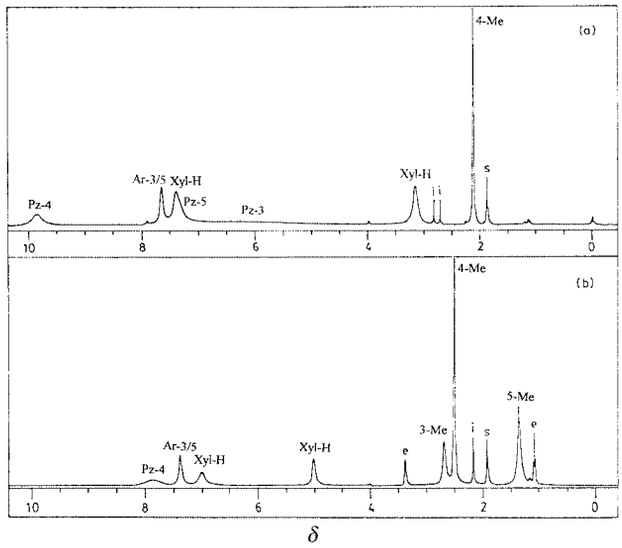


Fig. 3 400 MHz ^{1}H NMR spectra of (*a*) $[Cu_2(L)_2(OClO_3)_2]$ **1** and (*b*) $[Cu_2(L')_2(OClO_3)_2]$ **2** at room temperature in CD_3CN solution. The peaks marked e, i and s are due to diethyl ether, impurity and solvent, respectively. The abbreviations (Ar, Pz and Xyl) used in the assignments denote aromatic ring, pyrazole ring and xylyl protons respectively.

peak areas, proximity to the metal centres and comparison with "free" ligand spectra. We are a bit surprised to note the more spread out spectrum for **1**, even though it is more magnetically coupled than **2**. It is well documented[26,27] that the range is controlled by the strength of the antiferromagnetic coupling between the two copper centres, which is consistent with the notion that the isotropically shifted signal of a particular ligand proton is proportional to the magnetic susceptibility of the complex.

Redox properties

Complexes **1** and **2** display in MeCN solution at a platinum electrode (scan rate = 50 mV s^{-1}) three irreversible cathodic responses, with E_{pc} values (*vs.* SCE) of −0.02, −0.54 and −0.86 V for **1** and 0.00, −0.42 and −0.80 V for **2**. The first two reductive responses are assigned to Cu^{II}–Cu^{I} redox processes of two copper(II) centres. The most cathodic response is assigned to a Cu^{I}–Cu^{0} redox process, since an anodic scan following an initial cathodic scan is associated with a sharp feature at −0.2 V for **1** and −0.4 V for **2**, characteristic of desorption of electrogenerated copper(0) species.

The first reduction potentials are essentially identical; however, that for the second copper ion is different for the two compounds, with **2** being easy to reduce. We believe that this is due to the steric consequence of the pyrazole methyl substituents in complex **2**, as they relate to the substantial structural changes that will occur upon reduction/demetallation of one copper atom from the complexes, due to the different preferred[2d,6b] co-ordination polyhedra of Cu^{I} and Cu^{II}. For example, the pyrazole 5-methyl substituents might be expected to reduce the conformational flexibility of the two ligands. Alternatively, the 3-methyl substituents may force an increased tetrahedral distortion at the remaining copper ion once one metal centre has been lost from the complex. There is support for both these ideas from the complex chemistry of pyrazole-containing chelating ligands.[21]

Conclusion

We have synthesized two new diphenoxo-bridged copper(II) complexes in a non-macrocyclic/non-Schiff base ligand environment. The presence of a $\{Cu^{II}_2(\mu\text{-phenoxide})_2\}^{2+}$ structural unit with additional perchlorate co-ordination at each copper centre is clearly established by a crystal structural analysis of one such complex. The observed very strong antiferromagnetic exchange coupling between the two copper(II) centres results in sharp ^{1}H NMR spectra. Experiments to synthesize diphenoxo-bridged complexes with other first-row transition metal ions are under current investigation.

Acknowledgements

This work is supported by grants from the Council of Scientific & Industrial Research (CSIR) and Department of Science and Technology (DST), Government of India, New Delhi. R. G. gratefully acknowledges the award of a fellowship (SRF) by CSIR. The financial assistance of the National X-ray diffractometer facility by DST at this Department is gratefully acknowledged. We are very grateful for the referees' constructive suggestions during the revision stage.

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Paper 9/07250K