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An asymmetric dinuclear copper(II) complex with phenoxo and acetate bridges: Synthesis, structure and magnetic studies

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The dinuclear (μ_2-acetate)*bis*(μ_2-phenoxide)di-copper(II) complex, **1** with a tetradentate ligand, **L** (**L** = 2,4-di-*tert*-butyl-6-{[(2-dimethylaminoethyl)-(2-hydroxybenzyl)-amino]-methyl}-phenol) has been synthesized and characterized. The single crystal X-ray structure of the dinuclear complex was determined. Variable temperature magnetic susceptibility measurement showed that the two copper(II) centres are strongly anti-ferromagnetically coupled. The structural study revealed that the Cu–Cu distance (2.911 Å) is very close to the distance observed in dinuclear copper(II) acetate. The average Cu–O–Cu angles (~87°) are found to be the lowest amongst the examples reported so far.

1. Introduction

Bridged dinuclear copper(II) complexes have been the subject of continuing interest for chemists because of their magneto-structural properties. A considerable amount of work has been done in recent years to correlate the structure and magnetic properties of binuclear copper(II) complexes having alkoxo or hydroxo bridges [1,2]. An increase in the strength of anti-ferromagnetic coupling with an increasing Cu–O–Cu bridging angle has been observed in doubly bridged systems with a Cu–O–Cu angle in the range 90–105° and in single alkoxide or hydroxide bridged compounds with larger angles (120–135°) [3,4]. The linear relationship for the dihydroxide and alkoxide cases show that at an angle of around 97°, the point of experimental accidental orthogonality, the exchange integral approaches zero [3,4]. However, in the phenoxy bridged di-copper complexes, the linear least square fitting suggests that anti-ferromagnetic exchange will dominate at angle well below 97°, and the condition $-2J = 0\ \mathrm{cm}^{-1}$ should be achieved with a Cu–O–Cu angle of ~77°. However, this could not be proved experimentally as there are not many examples of copper complexes with a phenoxide bridged Cu–O–Cu angle less than 97° [5].

Here we report the synthesis, structure and magnetic study of an asymmetric di-copper(II) complex with two phenoxo and one acetate bridge, having Cu–O–Cu angles of 87.22° and 89.61°. This is perhaps the lowest Cu–O–Cu angle reported so far. The compound exhibits very strong anti-ferromagnetic coupling between the two Cu(II) centres, substantiating the theoretical results.

2. Results and discussion

The ligand **L** was prepared through a modified Mannich reaction of one equivalent of the phenol analogue, one equivalent of the amine and an excess (four equivalents) of formaldehyde (Scheme 1) [6–8]. The white solid product was precipitated out from the reaction mixture, and this was then washed with cold water and recrystallized from methanol to yield the pure product as a white microcrystalline powder (see Section 3). The formation of the ligand was authenticated by its FT-IR, ^{1}H and ^{13}C NMR spectral analysis (see Section 3).

The dinuclear copper(II) complex **1** was prepared by the reaction of equivalent amounts of copper(II) acetate tetrahydrate and the ligand in methanol solution. The dark brown reaction mixture was then kept for crystallization. The formation of the complex was confirmed by UV–Vis and FT-IR spectroscopic studies, and finally by its single crystal structure determination. The complex shows a room temperature magnetic moment, μ_{eff}, of 0.42 BM, which is much less than the expected spin only calculated value. This can be attributed to the very strong anti-ferromagnetic coupling between the two copper(II) centres *via* the phenoxo and acetate bridges [9].

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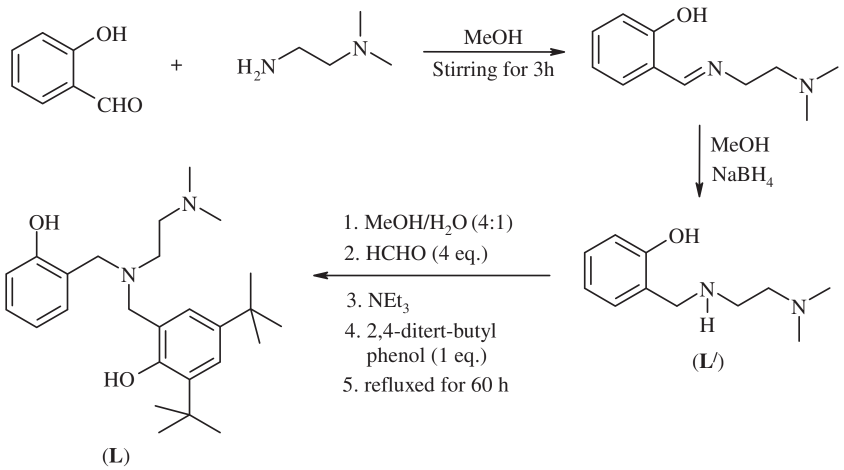

Scheme 1. Synthesis of the ligand.

2.1. Crystallography

A perspective ORTEP view, with the atom numbering scheme, of the dinuclear complex **1** is given in Fig. 1. The crystallographic data, selected bond lengths and angles are listed in Tables 1–3, respectively. In complex **1**, both the copper(II) centres adopt a square pyramidal geometry, however they have different coordination environments (Fig. 2). The deviation from the square plane for the Cu1 and Cu2 centres are 0.177 and 0.266 Å, respectively (Fig. 3). Two μ-phenolato oxygen atoms and one bidentate bridging (μ^2-η^1:η^2)H_3CCOO^- anion bridge the two copper(II) centres. For Cu1, the other two positions of the coordination sphere are occupied by two amine N-donors, whereas in Cu2, a separate η^2-acetate group completes the coordination sphere.

From the crystal structure, it has been found that in complex **1** the two inverted square pyramids are sharing a common apical-equatorial edge formed by the two μ-phenolato groups. For both the Cu(II) centres, the apical positions are occupied by the phenolato oxygen groups. It is clear from the structure that the O1-atom from one phenolato group is coordinated to Cu1 through the apical position, whereas it is equatorially coordinated to the Cu2 centre. Similarly, O2 is coordinated to Cu2 through the axial position; however it forms an equatorial coordination to the other Cu(II) centre (Fig. 2).

The Cu–$O_{phenolato}$ distances are observed to be in the range 1.9139–2.2622 Å. The axial Cu–$O_{phenolato}$ distances {2.2066(17) and 2.2622(17) Å} are found to be longer than the equatorial Cu–$O_{phenolato}$ ones {1.9450(16) and 1.9139(16) Å}, as expected [10–14]. The average Cu–$O_{acetate}$ distance for the (μ^2-η^1:η^2)H_3CCOO^- group is 1.9547 Å, which is shorter than the average Cu–$O_{acetate}$ distance {2.0095 Å} for the η^2-acetate group, as found in other cases [6]. The two Cu(II) centres are separated by 2.9111(4) Å. This is much shorter than the values for other reported complexes by Thompson et al. (e.g. ranging from 2.997 to 3.1184 Å) and is comparable to the value of 2.903(3) Å reported by Ray et al. [15–19]. It is worth mentioning that this Cu1–Cu2 distance is the short-

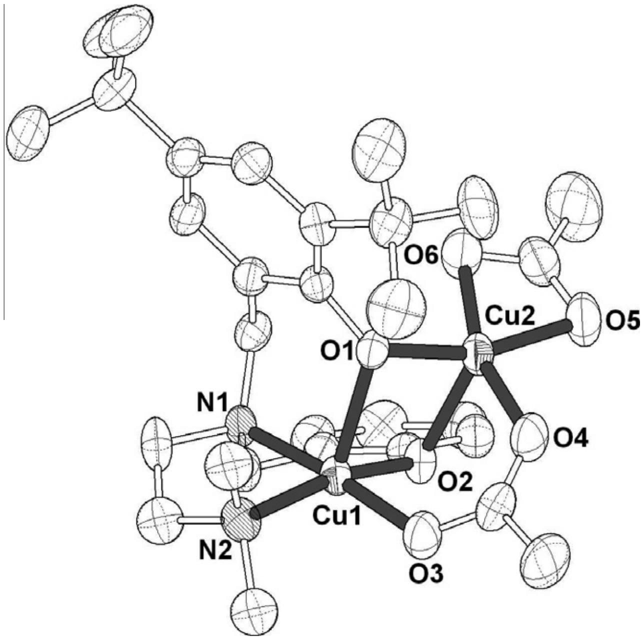

Fig. 1. ORTEP diagram for complex **1** (50% thermal ellipsoid plot). The atom numbering is shown only for the dinuclear core for clarity.

Table 1
Crystallographic data for complex **1**.

	Complex **1**
Formula	$C_{30}H_{45}Cu_2N_2O_6$
Molecular weight	664.76
Crystal system	monoclinic
Space group	$P2_1/c$
T (K)	296(2)
Wavelength (Å)	0.71073
a (Å)	9.1047(2)
b (Å)	16.8115(4)
c (Å)	22.0595(5)
β (°)	101.434(10)
V (Å^3)	3309.50(13)
Z	4
D_{calc} (mg m^{-3})	1.334
F(0 0 0)	1396
Total number of reflections	8136
Reflections [$I > 2\sigma(I)$]	5141
Max. 2θ (°)	28.39
Ranges (h, k, l)	$-12 \leqslant h \leqslant 12$ $-22 \leqslant k \leqslant 21$ $-28 \leqslant l \leqslant 29$
Complete to 2θ (%)	97.90
Refinement method	Full-matrix least-squares on F^2
wR_2 (all data)	0.1213
Goodness-of-fit (GOF) (F^2)	1.002
R indices [$I > 2\sigma(I)$]	0.0403
R indices (all data)	0.0684

Table 2
Selected bond lengths (Å).

Complex **1**	
Bond lengths (Å)	
Cu1–Cu2	2.9111(4)
Cu1–O2	1.9450(16)
Cu1–O3	1.9629(18)
Cu1–N1	2.004(2)
Cu1–N2	2.047(2)
Cu1–O1	2.2066(17)
Cu2–O1	1.9139(16)
Cu2–O4	1.9465(19)
Cu2–O6	1.992(2)
Cu2–O5	2.0270(19)
Cu2–O2	2.2622(17)
Cu2–C29	2.351(3)
O1–C1	1.353(3)
O2–C10	1.343(3)
O3–C27	1.267(3)
O4–C27	1.260(3)
O5–C29	1.251(3)
O6–C29	1.267(3)

Table 3
Selected bond angles (°).

Bond angles (°)	
O2–Cu1–O3	89.74(7)
O2–Cu1–N1	92.61(8)
O3–Cu1–N1	174.32(8)
O2–Cu1–N2	165.36(9)
N1–Cu1–O1	93.46(7)
N2–Cu1–O1	104.97(8)
O1–Cu2–O4	92.67(8)
O1–Cu2–O6	100.74(8)
O4–Cu2–O6	162.09(8)
O1–Cu2–O5	162.57(9)
O4–Cu2–O5	99.84(8)
O6–Cu2–O5	64.71(8)
O1–Cu2–O2	88.82(7)
O4–Cu2–O2	90.79(8)
O2–Cu1–N2	165.36(9)
O3–Cu1–N2	90.03(9)
N1–Cu1–N2	86.39(9)
O4–Cu2–O2	90.79(8)
O6–Cu2–O2	101.23(7)
O5–Cu2–O2	103.00(8)
C1–O1–Cu2	127.68(15)
C1–O1–Cu1	121.44(14)
Cu2–O1–Cu1	89.61(7)
C10–O2–Cu1	127.68(15)
C10–O2–Cu2	120.50(16)
Cu1–O2–Cu2	87.22(6)
O4–C27–O3	125.8(3)
O5–C29–O6	117.4(3)

est amongst the examples reported so far [15–19]. For a better comparison, the Cu–Cu distances for some reported complexes are given in Table 4. The distance between the two copper centres in dimeric copper(II) acetate is found to be 2.6–2.7 Å. The Cu–Cu distance in phenoxo bridged complexes becomes a little longer than a direct Cu–Cu distance because of steric reasons [20]. For open chain structures, this distance is reported to be ~4.1 Å [20].

The Cu1–O1–Cu2 bridging angle is found to be 89.61°, whereas the Cu1–O2–Cu2 angle is 87.22°, the smallest value found in this series of complexes. These values are found to vary from 91.6° to 109.4° [20,21]. The sum of the angles at the phenoxide oxygen atoms are 338.73° (O1) and 335.40° (O2), indicating a considerable degree of pyramidal oxygen distortion. It is worth mentioning that in $[Cu_2(L_1)(H_2O)_2]F_2(CH_3OH)_2$, the Cu–O–Cu angle is ~103.65(10)° and sum of the angles at the phenoxide oxygen is almost exactly 360° (O1, 359.8°), indicating no pyramidal oxygen distortion [9].

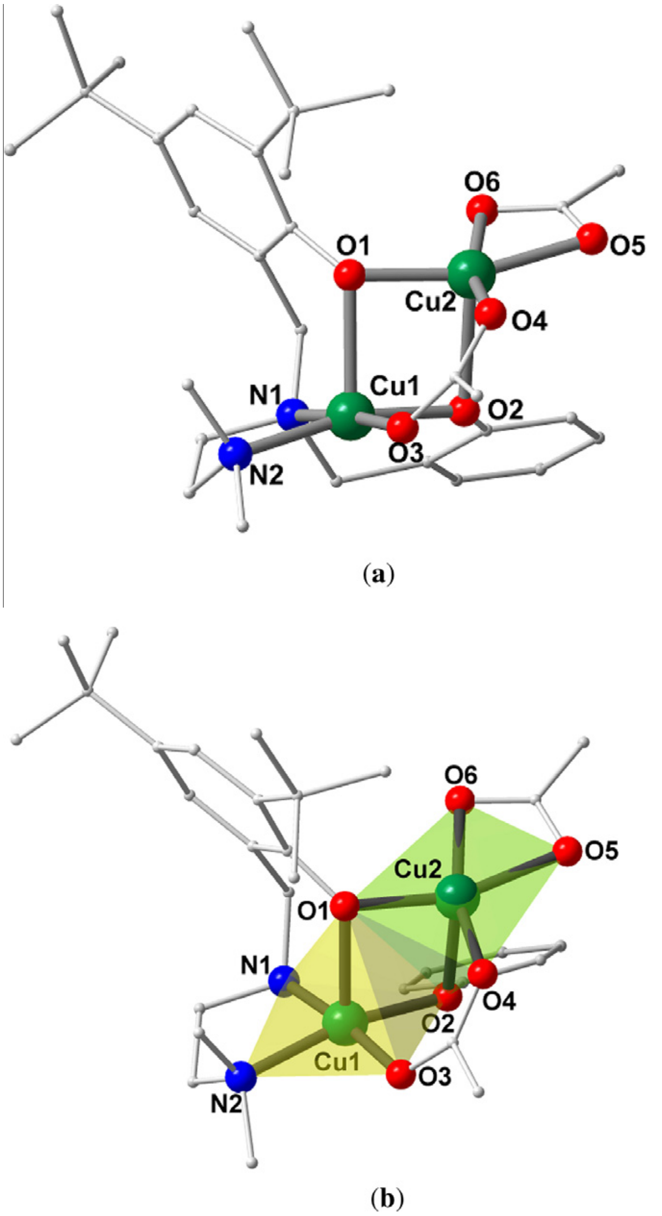

Fig. 2. (a) The two square pyramidal cores and (b) the inverted square pyramids sharing the axial-equatorial edge are shown.

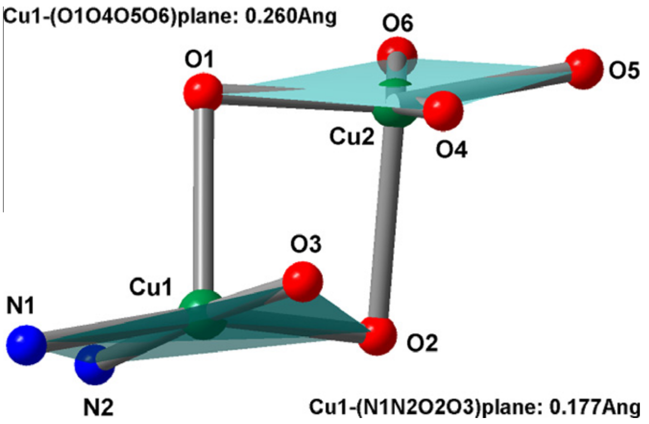

Fig. 3. The deviation of the copper(II) centres from the square plane in complex **1**.

Table 4
Structural and magnetic data for a series of related dinuclear copper(II) complexes **2**–**10**.

Compound	Cu–Cu (Å)	Cu–O–Cu (°)	Cu–O[a]	ϕ^{b} (°)	θ^{c} (°)	$-2J$ (cm^{-1})
2	3.154(2)	107.1(1)	1.945	56.8	333.5	185.4
3	3.491(2)	132.0(1)	1.905	5.8	358.8	174.4
4	3.495(2)	133.3(2)	1.904	18.7	358.9	179.2
5	3.492(2)	133.5(1)	1.910	6.3	356.9	163.6
6	3.395(7)	123.6(2)	2.003	45.5	n.a.	20.2
7	3.339(2)	120.1(2)	1.932	32.2	n.a.	55.6
8	3.642	143.7(2)	1.916	n.a.	n.a.	1000
9	3.331	129.1	1.873	n.a.	n.a.	586
10	3.401	121.3	1.929	162.6	346.6	595

2, $[Cu_2(L)(O_2CMe)]\cdot(C_3H_7NO)$ (L = 1,3-bis(2,hydroxy-3-meythoxybenzlidene)propan-2-ol) [24]; **3**, $[Cu_2(L_1)(O_2CMe)]1/2\cdot H_2O$ [19]; **4**, $[Cu_2(L_2)(O_2CMe)]1/2\cdot H_2O$ [31]; **5**, $[Cu_2(L_3)(O_2CMe)]\cdot H_2O$ [16]; **6**, $[Cu_2(OH)(O_2CMe)(H_2O)_2(dmen_2)][ClO_4]_2\cdot 2NaClO_4$ [32,33]; **7**, $[Cu_2(OH)(O_2CMe)(tmen_2)(ClO_4)_2]$ [3,33]; **8**, $[Cu_2(OH)(ClO_4)A](-ClO_4)_2\cdot CHCl_3$ (A: bi-nucleating macrocycle) [34]; **9**, $[Cu_2(L_1)(pyd)]BF_4\cdot H_2O$ [35]; **10**, $[Cu_2(-L_2)(prz)]$ [36]; n.a. = not available.

[a] Cu–O is the average distance between the copper and the bridging O atoms.

[b] Dihedral angle between coordination planes.

[c] Solid angle around the bridging oxygen atom.

A small deviation from the square pyramidal geometry is observed in the case of the Cu2 centre, compared to Cu1, and this is reflected in the O1–Cu1–O2 [89.66(7)°] and O1–Cu2–O2 [88.72(7)°] angles, which are very close to orthogonal.

The O1–C1 and O2–C10 distances, 1.353(3) and 1.343(3) Å respectively, are very close to the C–O single bond distance, indicating the phenolato character of the bridging O1 and O2 centres.

2.2. Magnetic properties

The room temperature magnetic moment of complex **1** is found to be very low (μ_{eff} = 0.42 BM), indicating the presence of very strong anti-ferromagnetic coupling between the two copper(II) centres. Variable temperature magnetic moment studies were carried out in the temperature range 77–300 K. The plot of the molar susceptibility versus temperature for complex **1** is shown in Fig. 4. The variable temperature susceptibility data (χ_M versus T) were fitted to the modified Bleaney–Bowers equation (Eq. (1)), considering the presence of monomeric impurities (ρ) [9,22,23], where N_α is the temperature independent paramagnetism.

$$\chi_M = \frac{2Ng^2\beta^2}{kT[3+\exp(-J/kT)]}(1-\rho) + \frac{Ng^2\beta^2}{2kT}\rho + N_\alpha \tag{1}$$

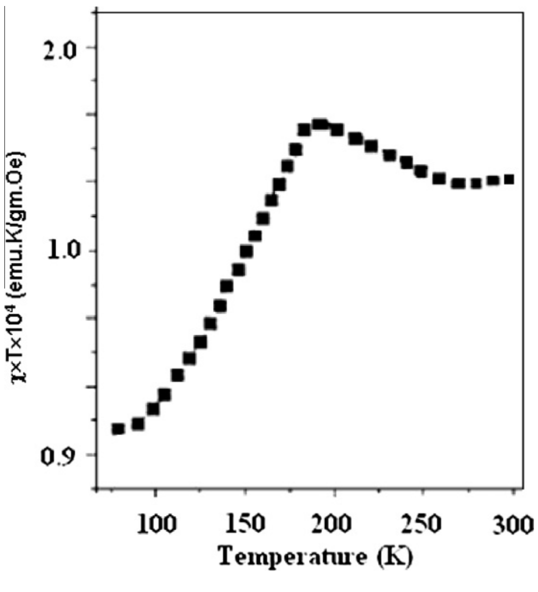

Fig. 4. Magnetic susceptibility versus temperature plot of complex **1**.

The isotropic exchange Hamiltonian used is $-2JS_1\cdot S_2$. The best data fit results into g = 2.08, $J = -398 \pm 10\ cm^{-1}$, ρ = 0.028 and $N_\alpha = 34 \times 10^{-6}$ emu. The observed results indicate the copper(II) centres present in complex **1** are strongly anti-ferromagnetically coupled with a large negative J value, which is usual for phenoxo bridged complexes (Table 4). The complex shows a maximum in magnetic susceptibility at ~185 K, which is typical of anti-ferromagnetic behaviour [24].

It is believed that several structural features of binuclear copper(II) complexes regulate the strength of exchange coupling interactions: (i) the dihedral angle between the two coordination planes, (ii) the planarity of the bonds around the bridging atom, and (iii) the Cu–O–Cu bridging angle [24–28]. Some interesting correlations between structural and magnetic parameters emerge from the data in Table 4 [24]. When we consider dinuclear copper(II) complexes with a single hydroxide bridge and a double hetero bridge (pyrazolate or pyridazine instead of an acetate bridge), it has been found that the structural properties of compounds **2**–**7** are not identical with those of the other compounds **8**–**10**, their anti-ferromagnetic super-exchange interactions being weaker (Table 4). This may show that the presence of a second bridging ligand affects the strength of the anti-ferromagnetic super-exchange interaction differently. In addition, although the second bridging ligands of **6** and **7** are the same as those of **2**–**5**, there is a significant difference in the $-2J$ values for these complexes.

The dihedral angle between the two coordination planes is considered to be a key factor in determining the magnitude of the spin-exchange coupling. However, as shown in Table 4, the dihedral angle decreases in the order **10** > **2** > **6** > **7** > **4** > **5** > **3**, while $-2J$ decreases in the order **10** > **2** > **4** > **3** > **5** > **7** > **6**. This indicates that the dihedral angle of the coordination sphere of unsymmetrical doubly bridged complexes may play only a minor role in determining the exchange interaction. The planarity of the bonds about the bridging oxygen atom has also been cited as factor influencing the nature of the spin-exchange interaction [29,30]. In fact, there is considerable variation in the planarity of the bonds around the bridging oxygen of the complexes under consideration. In the present case, the sum of the angles about the bridging oxygen atoms, on average, is ~337°, which is far from the idealized 360° angle expected for complete planarity. In the case of **4**, the sum of the three bond angles around the bridging oxygen is 358.9°, indicating the bonds around the oxygen are practically coplanar, in spite of the fact that the $-2J$ value is lower than the present complex. On the other hand, in the case of **5**, whose $-2J$ value is lower than **4**, the deviation from the plane is larger than **4**. Again this criterion by itself does not accurately predict the trend in the $-2J$ values. Perhaps the most widely accepted criterion for correlating structure and magnetism is the Cu–O–Cu bridging angle [29,30]. This factor has been invaluable in systematically correlating the degree of interaction in both singly and doubly alkoxide (or hydroxide) bridged copper complexes [37]. The Cu–O–Cu bridging angle decreases in the order **8** > **5** > **4** > **3** > **9** > **6** > **10** > **7** > **2**, while the value of $-2J$ does not decrease in the same order. But, in the symmetric bridged Cu(II) dinuclear complexes, for small values of Cu–O–Cu bridging angles (95–105°), Ruiz and co-workers observed that the Cu–O–Cu angle decreases in the same order as the value of $-2J$ [3]. The Cu–O bridging distance may also be a structural feature which determines the magnetic orbital overlaps, leading to the size of the singlet–triplet separation. The average distance between the copper and the bridging O-atom of the dinuclear copper(II) complexes in Table 4 are quite similar (<1.9 Å), but the $-2J$ values show significant differences. Particularly, in compounds **2**–**7**, which have the same kind of bridges, the increase in the average Cu–O bond lengths from 1.904 Å for **3** to 2.003 Å for **6** is connected with a decrease in the anti-ferromagnetic exchange-coupling constant from -179.2 to 220.2 cm^{-1}. The average Cu–O bond lengths decreases in the order **6** > **7** > **5** > **3** > **2** while the value of $-2J$ increases in the same order, i.e. **6** < **7** < **5** < **3**, except for the present complex.

2.3. Spectral properties

The UV–Vis spectrum of complex **1** is recorded in methanol solvent and is illustrated in Fig. 5. The complex exhibits intense absorptions at 221 and 286 nm (ε/mol^{-1} cm^2: 33255, 19560, respectively) in the UV-region. These are attributed to the intra-ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the visible region, a weak band is observed at λ_{max}, 735 nm (ε/mol^{-1} cm^2: 830) which presumably corresponds to the *d*–*d* transition. The absorption at ~421 nm (ε/mol^{-1} cm^2: 3100) is attributed to the phenolate → Cu(II) charge transfer [38].

The FT-IR spectrum of the complex **1** is recorded in a KBr pellet and is shown in Fig. 6. The strong bands at ~1603 and 1438 cm^{-1} are assigned to the $\nu_{(-COO)}$ symmetric and asymmetric stretching, respectively [20]. The difference between $\nu_{asym(COO-)}$ and $\nu_{sym(-COO-)}$, $\Delta\nu$, in the complex is about 165 cm^{-1}, which is a clear indication of the bidentate *syn*–*syn* bridging mode of the carboxylate [39–42]. The phenolic ν_{Ar-O} in the free ligand shows a strong band at ~1239 cm^{-1}. However, in the complex, this band is found at a lower frequency, at 1127 cm^{-1}, which can be attributed to coordination to the metal ions through the deprotonated phenolic oxygen atoms [43].

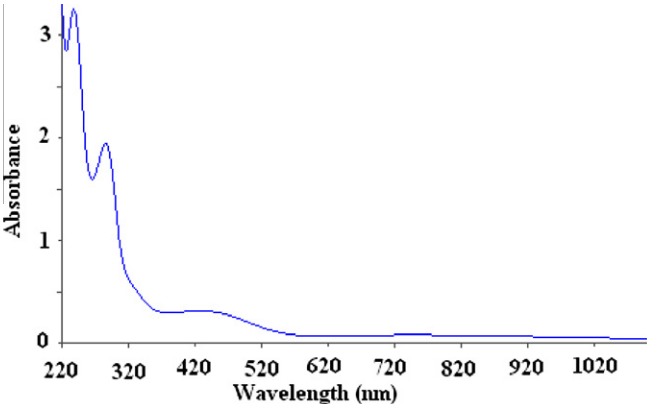

Fig. 5. UV–Vis spectrum of complex **1** in methanol solvent.

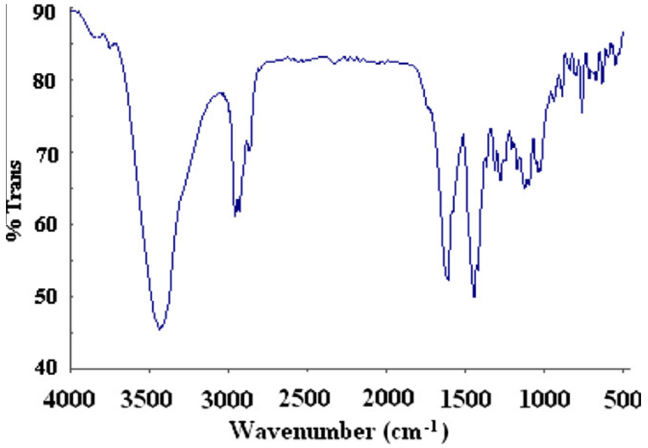

Fig. 6. FT-IR spectrum of complex **1** in KBr pellet.

3. Experimental

3.1. General

All reagents and solvents were purchased from commercial sources and were of reagent grade. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 25 UV–Vis spectrophotometer. FT-IR spectra were taken on a Perkin–Elmer spectrophotometer with samples prepared as KBr pellets. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. ^{1}H NMR spectra were obtained with a 400 MHz Varian FT spectrometer. Chemical shifts (ppm) were referenced either with an internal standard (Me_4Si) for organic compounds or to the residual solvent peaks. Elemental analyses were obtained from a Perkin–Elmer Series II Analyzer. The magnetic moment of complex was measured on a Cambridge Magnetic Balance. Variable temperature magnetic moment studies were carried out in a Lakeshore 7410 vibrating sample magnetometer.

Single crystals were grown by the slow diffusion followed by slow evaporation technique. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with fine focus 1.75 kW sealed tube Mo Kα radiation (λ = 0.71073 Å) at 273(3) K, with increasing ω (width 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software [44]. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [45]. Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least squares on F^2 using SHELXL-97 [46]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 for Windows [47].

3.2. Synthesis of the ligand

The Schiff base reaction was carried out using one equivalent of N,N-dimethylethane-1,2-diamine (1.76 g, 20 mmol) and an equivalent amount of salicylaldehyde (2.44 g, 20 mmol) in methanol medium. A yellow coloured imine was formed. The imine was reduced with 2.5 equivalents of sodium borohydride (1.90 g, 50 mmol). After the complete reduction, a colourless solution was obtained. The solution was stirred for 1 h. It was then neutralized with acetic acid to pH 7 and subsequently extracted with chloroform to afford **L**$^{/}$ (yield: 2.30 g, ~60%). One equivalent of formaldehyde (0.15 g, 5 mmol), one equivalent of triethylamine (0.50 g, 5 mmol) and one equivalent of 2,4-ditertiarybutylphenol (1.03 g, 5 mmol) were added to **L**$^{/}$ (0.97 g, 5 mmol) dissolved in a methanol–water mixture (1:4), and the resulting mixture was refluxed for 3 days at 60 °C. A white precipitate was observed, which was filtered, washed with water and dried (yield: 1.00 g, ~50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.160 (2H,t); 7.025 (1H,d); 6.89 (1H,d); 6.83 (1H,d); 6.744 (1H,t); 3.649 (2H,s); 3.576 (2H,s); 2.589 (4H,s); 2.317 (6H,s); 1.336 (9H,s); 1.239 (9H,s); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 157.2; 153.2; 140.6; 136.01; 130.8; 129.6; 124.7; 123.4; 122.6; 121.6; 119; 117.3; 57.8; 56.3; 55.2; 49.1; 45.1;

35.1; 34.2; 31.8; 29.7. FT-IR in KBr (cm^{-1}): 2963; 2868; 2829; 2780; 1613; 1582; 1485; 1364; 1279; 1239; 1165.

3.3. Preparation of the copper complex

$Cu_2(H_2O)_2(OAc)_4$ (0.199 g, 0.5 mmol) was dissolved in 15 ml methanol in a round bottom flask. To this blue solution, 262 mg (0.5 mmol) of the ligand was added with constant stirring, which was continued for 1 h. The blue colour of the solution immediately changed to dark green. The volume of the solution was reduced to 5 ml on a rotary evaporator. To this, 15 ml diethyl ether was added to make a layer and this was kept in the freezer overnight to yield a dark blue crystalline solid (yield: 0.21 g, ~64%). FT-IR in KBr (cm^{-1}): 3430(s); 2952(s); 1603(s); 1438(s); 1305(m); 1270(m); 1127(m); 1034(m). UV–Vis. λ_{max}, (nm): 221; 286; 421; 735.

3.4. Crystal data

CCDC No. 789702. $C_{30}H_{45}Cu_2N_2O_6$, $M = 664.76$, monoclinic, $a = 9.1047(2)$, $b = 16.8115(4)$, $c = 22.0595(5)$ Å, $\beta = 101.4340(10)°$, $V = 3309.50(13)$ Å^3, space group $P2_1/c$, $Z = 4$, $T = 296(2)$ K, l(Mo Kα) = 1.328 mm^{-1}, $F(0\,0\,0) = 1396$, Goodness-of-fit = 1.002; final R indices: $R_1 = 0.0403$ [$I > 2\sigma(I)$], $wR_2 = 0.1149$; R indices (all data): $R_1 = 0.0684$, $wR_2 = 0.1213$.

4. Conclusion

The present study demonstrates an example of a dinuclear copper(II) complex with two phenoxo and one acetate bridge. The coordination of the ligand around each of the two metal centres in complex **1** are found to be non-equivalent. A structural study reveals that the Cu–Cu distance (2.911 Å) is very close to the distance observed in dinuclear copper(II) acetate. The average Cu–O–Cu angles (~87°) are found to be the lowest amongst the examples reported so far. The variable temperature magnetic moment studies indicate a very strong anti-ferromagnetic coupling between the two copper centres. This can be attributed to the low Cu–O–Cu angle.

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Appendix A. Supplementary data

CCDC 789702 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://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; or e-mail: deposit@ccdc.cam.ac.uk.

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