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Binuclear copper(II) complexes containing phenols and catechols

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Abstract

The synthesis and characterisation of a series of binuclear copper(II) complexes of ligands formed by the condensation of substituted salicylaldehydes and 1,3-diamino-2-propanol (SalDplH$_3$) and 1,5-diamino-3-pentanol (SalDpeH$_3$) and their interaction with both phenols and catechols are reported. Spectroscopic and magnetic data suggest that the neutral phenols and catechols can bind to binuclear copper(II) complexes without actually coordinating to the copper atoms. The crystal and molecular structure of two binuclear copper(II) complexes have been solved. The μ-hydroxo bridged dicopper(II) complex of SalDpe^{3-}, [Cu$_2$SalDpe(OH)], $C_{19}H_{20}O_4N_2Cu_2$, **I**, having the space group *P*-1 and cell dimensions, $a=8.475(3)$, $b=15.727$, $c=6.999(2)$ Å, $\alpha=99.51(2)$, $\beta=92.84(3)$, $\gamma=77.66(2)°$ was solved for 1839 structure factors ($I>3.0\sigma(I)$) and $Z=2$, $R=4.2$, $R_w=4.3\%$. The compound consists of neutral molecules with an out-of-plane interaction from a copper in one binuclear unit to the hydroxo group of an adjoining molecule. The 4-ethylphenol adduct of the μ-(O,O')phenylacetate bridged dicopper(II) complex of SalDplH$_3$, [Cu$_2$SalDpl(Phenac)(4-Ethylphenol)], $C_{33}H_{31}N_2O_6Cu_2$, **II**, having the space group *P*-1 and cell dimensions, $a=11.872(2)$, $b=13.418(3)$, $c=11.046(2)$ Å, $\alpha=101.95(2)$, $\beta=103.65(1)$, $\gamma=113.35(1)°$ was solved for 3833 structure factors ($I>3.0\sigma(I)$) and $Z=2$, $R=4.1$, $R_w=4.3\%$. The 4-ethylphenol group is involved in a strong hydrogen bond to one of the phenolic oxygen donor atoms of the SalDpl^{3-} ligand and a weaker hydrogen bond to the adjoining oxygen donor atom of the bridging phenylacetate ion. The other phenolic oxygen donor atom is involved in an out-of-plane interaction to one of the copper atoms.

Keywords: Crystal structures; Copper complexes; Phenol complexes; Catechol complexes; Dinuclear complexes

1. Introduction

Tyrosinase is a monooxygenase found in microorganisms, plants and animals [1]. It catalyses the *o*-hydroxylation of monophenols to *o*-diphenols and the further oxidation of *o*-diphenols to *o*-quinones [2] (Fig. 1).

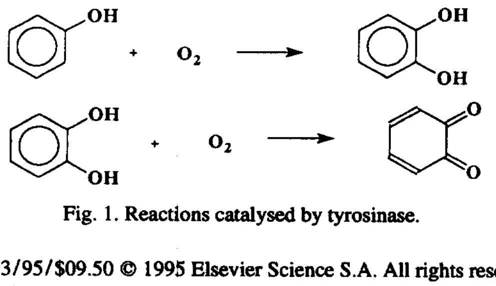

Fig. 1. Reactions catalysed by tyrosinase.

Spectroscopic studies [3] have shown that the coupled binuclear type III copper site in tyrosinase is similar to that in hemocyanins with the tyrosinase site being more accessible to larger substrate molecules. It has been suggested [4] that during the hydroxylation and oxidation reactions the phenol binds to one of the copper atoms and the catechol bridges between the two copper atoms as shown in Fig. 2.

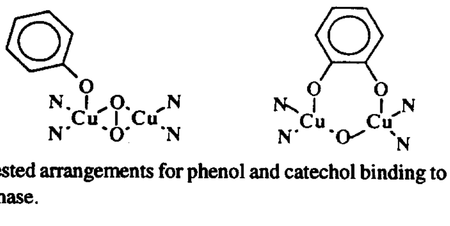

Fig. 2. Suggested arrangements for phenol and catechol binding to the active site in tyrosinase.

In early reports Tanaka [5] was able to observe evidence for addition complexes formed between phenols and monomeric ethylenediaminebis(salicylaldimine)copper(II), (CuSalen), and Baker et al. [6] obtained a crystal structure of the 4-nitrophenol adduct in which the phenol moiety was not bound directly to the copper atom but rather hydrogen bonded to the donor oxygen atoms. Earlier structures of adducts of

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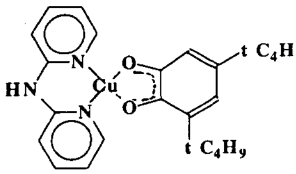


Fig. 3. Bonding arrangement of semiquinone in the model complex of Thompson and Calabrese [9].

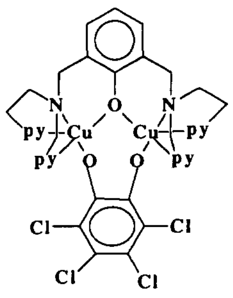


Fig. 4. Bonding arrangement of tetrachloro-*o*-quinone in the model complex of Karlin et al. [10].

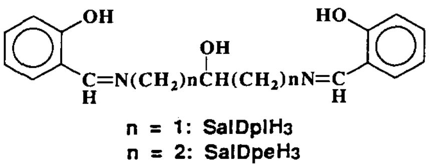


Fig. 5. Structural diagram for pentadentate ligands $SalDplH_3$ and $SalDpeH_3$.

water [7], and the methylammonium ion [8] provided some evidence that this could occur on a regular basis.

There have been several recent reports of model compounds of tyrosinase in which attempts have been made to bind phenols and/or catechols to copper complexes. Thompson and Calabrese [9] have synthesised a series of copper(II) 3,5-di-t-butyl-*o*-semiquinone complexes in which the partially oxidised catechol binds to the copper atom as a bidentate ligand (Fig. 3).

Karlin et al. [10] reacted their phenoxo bridged binuclear copper(I) complex with tetrachloro-*o*-benzoquinone and determined the structure of the catechol bridged complex formed (Fig. 4).

Casella et al. [11] have reacted a similar binuclear complex to that of Karlin et al. [10] with some phenols and catechols and have produced a reaction scheme which involves binding of phenols and catechols to their complex during the hydroxylation and oxidation reactions.

Described in this paper are the structure and properties of the 4-ethylphenol adduct of [Cu_2SalDpl(Phenylacetate)] along with the properties of other phenol and catechol adducts of this complex. In addition to this, the structure of [Cu_2SalDpe(OH)] will be described. While there have been a large number of structures reported for copper complexes based on Schiff base derivitives of 1,3-diaminopropan-2-ol, there have been considerably less structures reported of the copper complexes of the 1,5-diaminopentan-3-ol derivitive [12,13].

This paper will also describe the properties of a series of complexes of the types [Cu_2SalDpl$(Xcat)_{0.5}$] and [Cu_2SalDpe(XcatH)]. Structural diagarams for pentadentate ligands $SalDplH_3$ and $SalDpeH_3$ are shown in Fig. 5.

2. Experimental

2.1. Preparation of the Schiff base ligands

2.1.1. $SalDplH_3$

Salicylaldehyde (0.1 mol) and 1,3-diamino-2-propanol (0.05 mol) were refluxed in methanol (100 ml) for 30 min. The yellow Schiff base precipitated from solution on cooling.

2.1.2. $SalDpeH_3$

1,5-Diamino-3-pentanol·2HCl was prepared using the method of Murase et al. [14]. The Schiff base ligand was prepared by reacting the amine dihydrochloride with salicylaldehyde using the method of Mazurek et al. [12].

2.2. Copper complexes

2.2.1. [Cu_2SalDpl·Phenac]·H_2O

$SalDplH_3$ (4 g) dissolved in hot methanol (100 ml) and piperidine (2 ml), was added to a solution of copper phenylacetate·H_2O (9.5 g) dissolved in hot methanol (200 ml). The solution was boiled until the blue green complex started to precipitate.

2.2.2. [Cu_2SalDpl(Phenac)Y] (Y = phenols, catechols)

The phenol or catechol (0.006 mol) dissolved in dichloromethane (50 ml) was added to Cu_2SalDpl·Phenac·H_2O (0.004 mol) dissolved in dichloromethane (100 ml). Toluene (150 ml) was added to the solution and the solution boiled until the volume was reduced to approximately 150 ml. The adducts precipitated from solution on cooling.

2.2.3. [Cu_2SalDpl$(Xcat)_{0.5}$]

$SalDplH_3$ (3 g), $Cu(Sal)_2$ (6.2 g), $XcatH_2$ (2g) and piperidine (2 ml) were refluxed in methanol (100 ml) for 1 h or until the complex precipitated from solution.

2.2.4. [Cu_2SalDpe(OH)]·H_2O

$SalDpeH_3$ (3 g) was dissolved in hot methanol (100 ml) and piperidine (2 ml) and added to a solution of copper acetate monohydrate (3.7 g) dissolved in hot methanol (200 ml). The solution was boiled until the blue–green complex started to precipitate.

2.2.5. [Cu_2SalDpe(XcatH)]

The same method as in Section 2.2.3. was used with acetonitrile instead of methanol as the solvent. If methanol was used as the solvent, the product was always the hydroxo bridged binuclear compound.

Table 1
Crystallographic data for [Cu$_2$SalDpe(OH)], $C_{19}H_{20}O_4N_2Cu_2$ (I) and [Cu$_2$SalDpl(Phenac)(4-Ethylphenol)], $C_{33}H_{31}O_6N_2Cu_2$ (II)

	I	II
Formula	$C_{19}H_{20}O_4N_2Cu_2$	$C_{33}H_{31}O_6N_2Cu_2$
a (Å)	8.475(3)	11.872(2)
b (Å)	15.727(3)	13.418(3)
c (Å)	6.999(2)	11.046(2)
α (°)	99.51(2)	101.95(2)
β (°)	92.84(3)	103.65(1)
γ (°)	77.66(2)	113.35(1)
V (Å^3)	898.7(8)	1478.1(6)
Z	2	2
Formula weight	467.47	678.71
Space group	P-1	P-1
μ (cm^{-1})	24.00	14.89
T (°C)	22	22
λ (Å)	0.71069	0.71069
D (g cm^{-3})	1.727	1.525
Absorption corrections	Lorentz polarisation	Lorentz polarisation
Transmission factors	0.82–1.26	0.85–1.00
Secondary extinction		8.407×10^{-8}
R [a], R_w [b] (%)	4.2, 4.3	4.1, 4.3

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 4F_o^2/\sigma^2(F_o)^2$ and $\sigma^2(F_o)^2 = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$ where: S = scan rate; C = total integrated peak count; R = ratio of scan time to background counting time; B = total background count; Lp = Lorentz-polarisation factor; p = p-factor to down-weight intense reflections (0.03 for these structures).

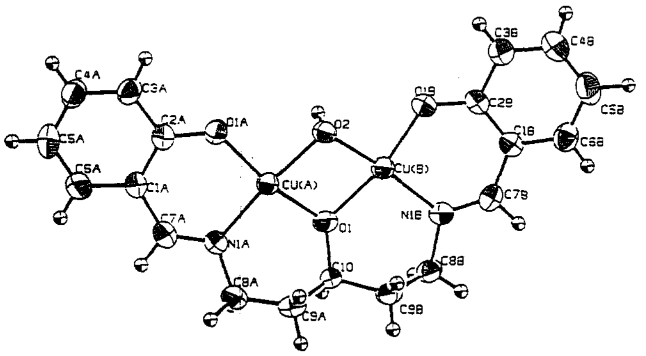


Fig. 6. Molecular diagram for [Cu$_2$SalDpe(OH)] showing numbering scheme used in Tables.

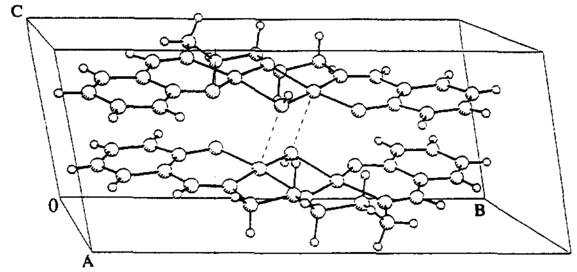


Fig. 7. Packing diagram for [Cu$_2$SalDpe(OH)].

2.3. X-ray methods

Data for [Cu$_2$SalDpe(OH)] (I) and [Cu$_2$SalDpl(Phenac)(4-Ethylphenol)] (II) were gathered with Mo Kα radiation on a Nicolet P3m automatic diffractometer using a graphite monochromator on the incident beam. Crystal, data collection and refinement data for the molecules were obtained by standard methods [15] and details are given in Table 1.

All structures were solved by direct methods [16] as implemented in the TEXSAN [17] system of computer programs. The structures were refined to convergence by full-matrix least-squares methods on a DEC 3120 workstation. All hydrogen atoms were found and their positional parameters refined. Atomic scattering factors used were those from the International Tables for X-ray Crystallography (1974) [18].

Tables S2 and S3 (see Section 6) list the refined coordinates and equivalent isotropic thermal paramenters for the selected atoms in I and II, respectively. Standard deviations, given in parentheses, are based solely on the least-squares results. Fig. 6 shows the atomic arrangement and Fig. 7 shows the packing arrangment in the unit cell in the binuclear copper unit for I, while Figs. 8 and 9 give the atomic arrangements for the binuclear unit and dimer of binuclear units for II.

2.4. Elemental analyses

Carbon, hydrogen and nitrogen analyses were carried out by Amdel Microanalytical Services, Melbourne, Australia, the Chemical and Microanalytical Services, North Essendon, Australia and the Microanalytical Laboratory at the Australian National University, Canberra, Australia.

2.5. Spectra

2.5.1. Visible spectra

Visible spectra were recorded on a Cary-17 spectrophotometer or a Shimadzu UV-265 spectrophotometer. Solid state spectra were run with the complexes suspended in nujol on filter paper.

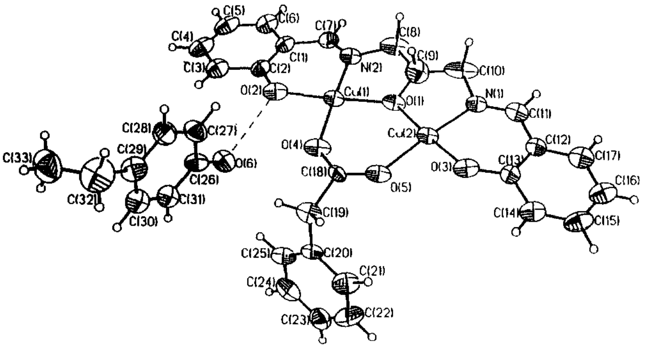


Fig. 8. Molecular diagram for [Cu$_2$SalDpl(Phenac)(4-Ethylphenol)] showing the hydrogen bonding interaction between the 4-ethylphenol and one of the ligand oxygen donor atoms. Also shown is the numbering scheme used in the Tables.

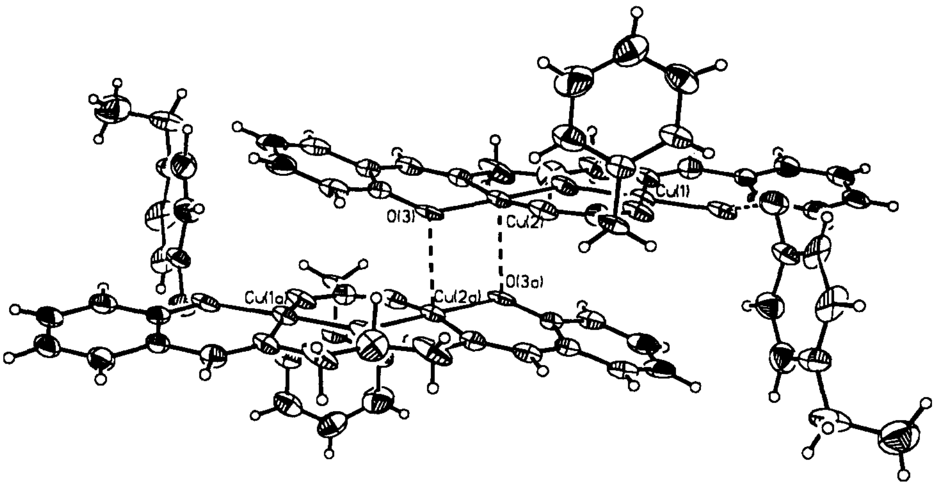


Fig. 9. Packing diagram for [Cu_2SalDpl(Phenac)(4-Ethylphenol)].

2.5.2. Infrared spectra

Infrared spectra were recorded in potassium bromide pellets on a Perkin Elmer 1430 spectrophotometer or a Bio-Rad FTS 60 spectrophotometer or in nujol mulls on a Perkin Elmer 283B spectrometer.

2.6. Magnetic measurements

Room temperature and 80–300 K magnetic moments were carried out using a Gouy Balance. In the range 10–100 K, measurements were carried out on a S.H.E. SQUID VTS susceptometer.

3. Results

3.1. Structures of the complexes

3.1.1. Structure of [Cu_2SalDpe(OH)]

The structure of this compound shows comparatively weak out-of-plane bonding between one of the copper atoms from each binuclear unit thus effectively making this compound a dimer of binuclear units.

Table S2 contains the positional parameters for this compound and Table 2 contains the metrical parameters. Structure factor tables have been deposited (see Section 6).

3.1.2. Structure of [Cu_2SalDpl(Phenac)(4-Ethylphenol)]

The structure of this compound shows strong hydrogen bonding interactions between the phenolic oxygen atom of 4-ethylphenol and one of the phenolic oxygen donor atoms of the $SalDpl^{3-}$ ligand. It also shows a comparatively weak out-of-plane bonding (see Fig. 9) between one of the copper atoms from each binuclear unit thus effectively making this also a dimer of binuclear units.

Table S3 contains the positional parameters for this compound and Table 3 contains the metrical parameters. Structure factor tables have been deposited (see Section 6).

3.1.3. [Cu_2SalDpl$(Xcat)_{0.5}$] and [Cu_2SalDpe(XCatH)]

Attempts to grow crystals of these complexes were unsuccessful. In most attempts, brown powders slowly deposited from solution. These brown products are probably oxidation products of the catechols. It may be possible to grow suitable crystals under an inert atmosphere.

3.2. Infrared spectra

The infrared and visible spectral properties for this series of compounds are summarised in Table 4. The complexes all contain a ν(C=N) band in the 1617–1640 cm^{-1} region. This band is asymmetric in the catechol bridged complexes of the ligands $SalDpl^{3-}$ and $SalDpe^{3-}$ and is clearly split into two bands in [Cu_2SalDpl·(3-OCH_3Cat$)_{0.5}$]. This splitting is probably due to the steric effect of the bulky methoxy group close to one of the two copper atoms and the associated imine ligand.

The phenol and catechol adducts of the phenylacetate bridged binuclear complexes all contain a ν(OH) band in the 3200–3450 cm^{-1} region which can be assigned to the phenolic group which is hydrogen bonded to the ligand. Some of the complexes which also contain water have an additional ν(OH) band at ~3200 cm^{-1}.

The infrared spectra of all the complexes in the 1800–1400 cm^{-1} region are similar. There does not appear to be any evidence for partial or complete oxidation of the catechols to the semi-quinone or quinone form of the catechols in these complexes.

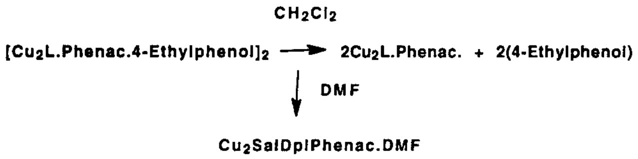
3.3. Visible spectra

3.3.1. [Cu_2SalDpl(Phenac)]·Y

Spectral and structural studies on complexes of the type [Cu_2SalDpl·Carboxylate] [19] have shown that complexes with two four-coordinate square-planar copper atoms ($CuNO_3$) have a spectral band at ~620 nm while complexes with one four-coordinate square-planar copper atom and one five-coordinate square pyramidal copper atom ($CuNO_4$) have a spectral band at ~ 640 nm.

Cu_2SalPDpl · Phenac · H_2O has a spectral band at 620 nm which is consistant with a structure in which both copper atoms are square planar. The spectra of the complex in dichloromethane indicates that this structure is unchanged in that solvent. The shift in the spectral band to 640 nm in dimethylformamide indicates that a dimethylformamide molecule binds to one of the two copper atoms in a similar manner to that in [Cu_2SalDpl(Pivalate)(DMF)] [20].

Cu_2SalDpl · Phenac · 4-C_2H_5Phenol has a solid state band at 640 nm which is consistant with its structure which contains one four-coordinate and one five-coordinate copper atom. When the complex is dissolved in dichloromethane, the spectral band shifts to 625 nm indicating that the dimer of binuclear units breaks down to the binuclear unit which contains two square planar copper atoms. When the complex is dissolved in dimethylformamide, the spectral band remains at 640 nm indicating that either the dimeric nature of the complex is maintained in dimethylformamide solution or more likely that a dimethylformamide molecule coordinates to one of the two copper atoms in the binuclear species (Scheme 1).



Scheme 1.

The position of the spectral band in the solid state spectra of the remaining phenol and catechol adducts of the phenylacetate bridged binuclear complex, with the possible exception of the 4-fluorophenol adduct, indicates that these complexes are most likely simple binuclear units with both copper atoms in a square planar environment. The solution spectra of the adducts in dichloromethane are almost identical with a spectral band at 625 nm which is not surprising since the phenols and catechols do not coordinate to the copper atoms. The same situation occurs in dimethylformamide where the adducts have a spectral band at 640 nm.

3.3.2. [Cu_2SalDpe(OH) · H_2O)]

The binuclear copper(II) hydroxo bridged complex of the ligand Sal$DpeH_3$ precipitates from solution as the monohydrate. The water molecule is lost during the recrystallisation method used to obtain the crystals used in the structure determination. Previous spectral studies [19] showed that the Sal$DpeH_3$ ligand produces a stronger ligand field in the binuclear copper(II) complexes than does the Sal$DplH_3$ ligand.

Table 2
Selected metrical parameters involving non-hydrogen atoms for [Cu_2SalDpe(OH)] (**I**)

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Cu(A)	O1	1.943(4)	Cu(A)	O1A	1.908(4)
Cu(A)	O2	1.930(4)	Cu(A)	N1A	1.952(4)
Cu(B)	O1	1.946(4)	Cu(B)	O1B	1.893(4)
Cu(B)	O2	1.933(4)	Cu(B)	N1B	1.941(5)
O1	C10	1.422(6)	O1A	C2A	1.310(6)
O1B	C2B	1.325(6)	N1A	C7A	1.269(2)
N1A	C8A	1.485(7)	N1B	C7B	1.287(7)
N1B	C8B	1.485(7)			
Cu(A)	Cu(B)	3.362(1)	[a]		
Cu(A)	Cu(A)	3.428(2)	[b]		
Cu(A)	O2	2.521(4)	[c]		

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O1	Cu(A)	O1A	162.7(2)	O1	Cu(A)	O2	79.0(2)
O1	Cu(A)	N1A	95.8(2)	O1A	Cu(A)	O2	90.6(2)
O1A	Cu(A)	N1A	95.0(2)	O2	Cu(A)	N1A	174.4(2)
O1	Cu(B)	O1B	166.1(2)	O1	Cu(B)	O2	78.8(2)
O1	Cu(B)	N1B	97.4(2)	O1B	Cu(B)	O2	89.9(2)
O1B	Cu(B)	N1B	95.2(2)	O2	Cu(B)	N1B	168.6(2)
Cu(A)	O1	Cu(B)	100.7(2)	Cu(A)	O1	C10	125.9(3)
Cu(B)	O1	C10	127.2(3)	Cu(A)	O1A	C2A	125.4(4)
Cu(B)	O1B	C2B	126.2(4)	Cu(A)	O2	Cu(B)	101.6(2)
Cu(A)	N1A	C7A	122.3(4)	Cu(A)	N1A	C8A	120.0(4)
Cu(B)	N1B	C7B	123.0(4)	Cu(B)	N1B	C8B	118.3(4)
O1	C10	C9A	110.9(5)	O1	C10	C9B	111.0(4)

E.s.d.s in the least significant figure are given in parentheses.

[a] $1-x, 1-y, 1-z$.

[b] $1-x, 1-y, 1-z$.

[c] $1-x, 1-y, 1-z$.

Table

Table 3

Selected metrical parameters involving the non-hydrogen atoms for [Cu$_2$SalDpl(Phenac)(4-Ethylphenol)] (**II**)

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Cu1	O1	1.906(3)	Cu1	O2	1.913(3)
Cu1	O4	1.924(3)	Cu1	N2	1.926(3)
Cu2	O1	1.924(3)	Cu2	O3	1.909(3)
Cu2	O5	1.954(3)	Cu2	N1	1.930(3)
O1	C9	1.371(5)	O2	C2	1.320(5)
O3	C13	1.328(5)	O4	C18	1.250(5)
O5	C18	1.251(5)	O6	C26	1.367(5)
Cu2	Cu2	3.185(1)	[a]		
O2	O6	2.745(4)	[b]		

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O1	Cu1	O2	177.3(1)	O1	Cu1	N2	84.1(1)
O1	Cu1	O4	95.6(1)	O2	Cu1	O4	87.0(1)
O2	Cu1	N2	93.2(1)	O4	Cu1	N2	172.7(1)
O1	Cu2	O3	176.7(1)	O1	Cu2	O5	94.1(1)
O1	Cu2	N1	84.3(1)	O3	Cu2	O5	89.2(1)
O3	Cu2	N1	92.4(1)	O5	Cu2	N1	170.8(1)
Cu1	O1	Cu2	131.1(1)	Cu1	O1	C9	114.0(3)
Cu1	O2	C2	126.5(3)	Cu1	O4	C18	134.8(3)
Cu1	N2	C7	127.1(3)	Cu1	N2	C8	113.5(3)
Cu2	O1	C9	113.5(3)	Cu2	O3	C13	125.0(3)
Cu2	O5	C18	135.1(3)	Cu2	N1	C10	112.1(3)
Cu2	N1	C11	127.2(3)	O1	C9	C8	117.2(4)
O1	C9	C10	117.0(4)	O4	C18	O5	127.4(4)
O4	C18	C19	116.6(4)	O5	C18	C19	115.9(4)

E.s.d.s in the least significant figures are given in parentheses.

[a] $1-x, 1-y, 1-z$.

[b] $x, y, z-1$.

Table 4

Spectroscopic properties of phenol and catechol adducts of binuclear copper complexes

Complex	Infrared [a]		Visible [b,c]		
	ν(OH)	ν(C=N)	Solid	CH$_2$Cl$_2$	DMF
[Cu$_2$L^1(Phenac)]·H$_2$O	3450	1630	620	625(515)	640(423)
[Cu$_2$L^1(Phenac)(PhOH)]·Tol	3300	1635	620	625(495)	640(387)
[Cu$_2$L^1(Phenac)(4-FPhOH)]	3450	1640	630	625(540)	640(413)
[Cu$_2$L^1(Phenac)(2-ClPhOH)]	3450	1630	615	625(430)	640(413)
[Cu$_2$L^1(Phenac)(4-ClPhOH)]	3200	1640	620	630(516)	640(380)
[Cu$_2$L^1(Phenac)(4-C$_2$H$_5$PhOH)]	3450	1637	640	625(511)	640(380)
[Cu$_2$L^1(Phenac)(CatH$_2$)]	3200	1635	620	625(511)	645(432)
[Cu$_2$L^1(Phenac)(4-CH$_3$CatH$_2$)]·2H$_2$O	3250 3400	1637	615	620(519)	640(409)
[Cu$_2$L^1(Phenac)(4-NO$_2$CatH$_2$)]·2H$_2$O	3200 3400	1635	615	620(455)	640(323)
[Cu$_2$L^1(Cat)$_{0.5}$]·(H$_2$O)$_{0.5}$		1635	630	620(265)	630(391)
[Cu$_2$L^1(3-CH$_3$OCat)$_{0.5}$]		1639 1631	620	625(368)	610(300)
[Cu$_2$L^{1}3-CH$_3$Cat)$_{0.5}$]		1634	655	590(330)	600(210)
[Cu$_2$L^1(4-CH$_3$Cat)$_{0.5}$]·(H$_2$O)$_{0.5}$	3310	1634	625	610(310)	620(210)
[Cu$_2$L^2(CatH)](H$_2$O)$_{0.5}$		1625	590(sh) [d]	570(sh)	570(sh)
[Cu$_2$L^2(4-NO$_2$CatH)]		1617	615	605(299)	620(173)
[Cu$_2$L^2(OH)]H$_2$O	3385	1634	610	585(434)	583(325)

[a] Measured in cm^{-1}.

[b] Measured in nm.

[c] Concentrations in the range 3×10^{-4} to 1×10^{-3}; extinction coefficients in brackets.

[d] sh = shoulder.

Table 5
Analyses and magnetic data

Complex		C (%)	H (%)	N (%)	μ [a] (temp. range K)
$[Cu_2L^1(Phenac)]\cdot H_2O$ [b,c]	c	52.17	4.20	4.87	1.28–1.72 (84–300)
	f	52.01	4.43	4.85	
$[Cu_2L^1(Phenac)(PhOH)]Tol(_{0.5})$ [d,e]	c	63.11	5.10	3.55	0.19–1.61 (11–300)
	f	63.01	4.88	3.57	
$[Cu_2L^1(Phenac)(4\text{-}FPhOH)]$	c	55.60	4.06	4.18	0.21–1.74 (11–300)
	f	56.14	4.17	4.18	
$[Cu_2L^1(Phenac)(2\text{-}ClPhOH)]$	c	54.27	3.97	4.08	0.20–1.71 (11–300)
	f	54.28	3.75	4.08	
$[Cu_2L^1(Phenac)(4\text{-}ClPhOH)]$	c	54.27	3.97	4.08	0.19–1.66 (11–300)
	f	53.88	4.08	3.82	
$[Cu_2L^1(Phenac)(4\text{-}C_2H_5PhOH)]$	c	58.31	4.75	4.12	0.21–1.79 (11–300)
	f	57.63	4.70	4.01	
$[Cu_2L^1(Phenac)(CatH_2)]$ [f]	c	55.77	4.24	4.20	0.22–1.70 (11–300)
	f	55.46	4.00	4.20	
$[Cu_2L^1(Phenac)(4\text{-}CH_3CatH_2)]\cdot 2H_2O$	c	53.55	4.78	3.90	1.10–1.99 (82–300)
	f	53.40	4.40	3.66	
$[Cu_2L^1(Phenac)(4\text{-}NO_2CatH_2)]\cdot 2H_2O$	c	49.73	4.17	5.61	0.91–1.80 (81–300)
	f	49.94	3.57	5.29	
$[Cu_2L^1(Cat)_{0.5}]\cdot(H_2O)_{0.5}$	c	49.98	3.74	5.77	1.78–2.06 (80–300)
	f	49.65	3.59	5.80	
$[Cu_2L^1(3\text{-}CH_3OCat)_{0.5}]$	c	50.10	3.64	5.70	1.73–2.03 (80–300)
	f	50.20	3.74	5.74	
$[Cu_2L^1(3\text{-}CH_3Cat)_{0.5}]$	c	50.93	3.75	5.79	1.62–1.99 (80–300)
	f	51.09	3.84	5.87	
$[Cu_2L^1(4\text{-}CH_3Cat)_{0.5}]\cdot(H_2O)_{0.5}$	c	50.00	3.89	5.69	1.55–1.96 (90–300)
	f	49.73	3.57	5.45	
$[Cu_2L^2(CatH)]\cdot(H_2O)_{0.5}$ [g]	c	52.81	4.43	4.93	0.40–0.82 (80–300)
$[Cu_2L^2(4\text{-}NO_2CatH)]$	c	49.67	3.83	6.95	0.48–1.09 (80–300)
	f	49.65	4.22	7.35	
$[Cu_2L^2(OH)]H_2O$	c	47.01	4.57	5.70	1.48–1.57 (90–300)
	f	46.58	4.63	5.59	

[a] Measured in Bohr magnetons; temperature range in brackets.
[b] L^1 = Saldpl^{3-}.
[c] Phenac = phenylacetate.
[d] PhOH = phenol.
[e] Tol = toluene.
[f] $CatH_2$ = catechol.
[g] L^2 = SalDpe^{3-}.

This results in the spectral bands of the SalDpe^{3-} copper complexes occuring at lower wavelengths. The monohydrate has a band at 610 nm in the solid state and at 585 nm in dichloromethane and dimethylformamide. This suggests that the compound has one four-coordinate and one five-coordinate copper atom in the solid state and two four-coordinate copper atoms in solution. The compound in the solid state would seem either to have the same dimeric structure as does the anhydrous compound or may have the water molecule bound to one of the two copper atoms. Since the compound does not appear to bind the oxygen donor ligand dimethylformamide in solution it seems likely that the compound is a dimer in the solid state with the water molecule present in the crystal lattice.

3.3.3. *[Cu_2SalDpe(XCatH)] and [Cu_2SalDPl$(XCat)_{0.5}$]*

Interpretation of the visible spectra of these catechol bridged complexes is more difficult. In the catechol bridged complex of the SalDpe^{3-} ligand, an intense charge transfer band overlaps with the band at ~600 nm making it difficult to identify spectral shifts. There are no consistant trends in the spectra of the remaining catechol bridged complexes on changing from the solid state to solution. Crystal structural data will be needed to assist in the interpretation of these spectra.

3.4. *Magnetic measurements*

3.4.1. *[Cu_2SalDpl·(Phenac)·Y]*

Variable temperature magnetic measurements are summarised in Table 5. These measurements on [Cu_2SalDpl(Phenac)(H_2O)] and its phenol and catechol adducts show the presence of weak antiferromagnetic interactions between the two copper atoms. The magnetic moments vary from ~0.2 B.M. at 11 K to a value close to the spin only value (1.73 B.M.) at 300 K. The magnetic moments appear to be in a similar range to that reported [20] for the acetate and propionate bridged copper(II) complexes

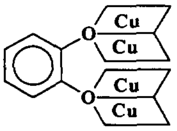


Fig. 10. Schematic diagram showing how the copper donor planes are forced out of planarity by the steric constraints of a bridging catechol ligand.

of the same ligand. The amount of antiferromagnetic interaction does not change significantly in the series of compounds which is not surprising since they all appear to have a similar structure in which the phenols and catechols are not coordinated to the copper atom.

3.4.2. [$Cu_2SalDpl(Xcat)_{0.5}$]

The antiferromagnetic interaction between the copper atoms in these complexes is much weaker than that in the phenylacetate bridged complexes with the magnetic moments being about 2.0 B.M. at 300 K and ~1.7 B.M. at 80 K. This type of magnetic behaviour is similar to that observed in $Cu_2SalDpl \cdot Pivalate \cdot DMF$ [20] where the dihedral angle for the planes between the copper planes is 60.5°. This is in marked contrast to the strong interactions found in complexes such as [Cu_2ESalDpl(Propionate)] [20] and in [Cu_2SalDpl(Acetate)] [20] where smaller dihedral angles of 6.5 and 7.6° are found, respectively. The stoichiometry of these complexes with one catechol per two binuclear units suggests that the catechol bridges these two binuclear units. Presumably the copper planes are forced out of planarity (increasing the dihedral angle) by the steric constraints of the bridging catechol group (Fig. 10). The resulting increase in the dihedral angle would then produce the weak antiferromagnetic interaction observed in these complexes.

3.4.3. [$Cu_2SalDpe(XcatH)$]

The antiferromagnetic interaction in binuclear copper(II) complexes with the ligand $SalDpe^{3-}$ is usually much greater than that in the corresponding $SalDpl^{3-}$ complexes regardless of the nature of the exogenous bridge [19]. This increased antiferromagnetic interaction is also observed in the complexes in this paper with the magnetic moments being in the range ~1.0 B.M. at 330 K to ~0.5 B.M. at 80 K. The greater flexibility of the longer alkyl groups in the ligand may make it easier for the ligand to reduce the dihedral angle between the two copper planes thus maximising the magnetic interaction.

3.4.4. [$Cu_2SalDpe(OH)$]

The crystal structure of this compound has shown that it should be considered as a tetramer made up of binuclear units linked by out-of-plane bonding between the copper of one binuclear unit and the μ-hydroxy moiety of an adjoining unit. Because of the dimensions involved there is a strong antiferromagnetic interaction between the copper atoms in the binuclear subunits and much weaker antiferromagnetic interactions between binuclear units. The small dihedral angle between the two donor planes in the binuclear subunits also indicates that the antiferromagnetic interactions between the copper atoms in such a subunit should be large.

4. Discussion

4.1. Structures of the complexes

4.1.1. [$Cu_2SalDpe(OH)$]

Fig. 6 shows the presence of a pentadentate binucleating ligand in compound **I**. The copper atoms are bridged by the oxygen atoms O(1) and O(2) from the secondary alkoxo substituent of the ligand and the hydroxo group, respectively. The NO_3 donor atom sets about each copper atom are essentially planar with Cu(A) and Cu(B) displaced by 0.102 and 0.031 Å respectively from these planes. However the deviations of the donor atoms of each set from planarity is much greater (up to 0.162 Å for O(2) from the O(1), O(1B), O(2), N(B) set than found in the analogous complex [12] formed from pyridine-2-carboxaldehyde in the place of salicylaldehyde (**III**). These planes themselves are also almost coplanar with a dihedral angle of only 2.8° in contrast to that found for **III** [12], where the dihedral angle between the planes is 13.0°.

In fact, the atoms Cu(A), Cu(B), O(1) and O(2) are in a plane with Cu(A), O(1A), N(1A) and Cu(B), O(1B), N(1B) planes making dihedral angles of 13.9 and 13.0°, respectively with this plane. This is in marked contrast to the situation in **III** where the two sets of donor atoms (O(1), O(2), N(2) and N(4) around Cu(1) and O(1), O(2), N(1) and N(3) around Cu(2)) are coplanar but with a dihedral angle of 12.8° between the planes and Cu(1) and Cu(2) displaced by 0.179 and 0.126 Å, respectively, from these planes.

In the ligand backbone the deviations of the carbon bond angles from regular tetrahedron (largest deviation from 109.5° is found for the C(8A) C(9A) C(10) angle at 116.6(5)°) are markedly less than found in **III** where angles of up to 126.3(8)° are found. Thus in **I** the angular strain appears to be manifested in the larger deviations from planarity whereas in **III** this strain manifests itself in large deviations of the angles involving the ligand backbone.

In the present complex, Cu(A) has the common 4 + 1 arrangement of donor atoms with a weak out-of-plane bond with the O(2) of a neighboring ligand at 2.521(4) Å, while Cu(B) has only four donor atoms. This is longer than analogous Cu–O bond in **III** (2.421(1) Å). As a result of these out-of-plane interactions, the overall structure involves pairs of binucleating units as seen in Fig. 9.

In **I** the shortest bond lengths are to the phenolic atoms (Cu(A)–O(1A), 1.908(4) Å; Cu(B)–O(1B), 1.893(4) Å) with intermediate lengths involving the bridging hydroxo O(2) (Cu(A)–O(2), 1.930(4) Å; Cu(B)–O(2), 1.933(4) Å) and longer bond lengths involving the bridging alkoxide O(1) (Cu(A)–O(1), 1.943(4) Å; Cu(B)–O(1), 1.946(4) Å). This again is in contrast to the situation in **III** where the shortest copper–donor bond lengths are to the bridging alkoxide oxygen (Cu(1)–O(1), 1.903(3) Å; Cu(2)–O(1), 1.907(3) Å). In view of this difference in coordination number for the two copper atoms there is remarkable similarity in the metrical parameters of the copper atoms involving similar donor atoms.

4.1.2. *[Cu_2SalDpl(Phenac)(4-Ethylphenol)]*

This compound consists of a binuclear SalDpl^{3-} ligand bridging two copper atoms with the coordination for each copper completed by a bridging phenylacetate moiety.

The metrical parameters involving the copper atoms in the complex are similar to those found in other [12–14,19–23] binuclear copper compounds based on the pentanuclear ligand SalDpl^{3-}. Bond lengths involving the copper atoms fall into four groups. Short bonds to the alkoxo oxygen (Cu(1)–O(1), 1.906(3) Å; Cu(2)–O(1), 1.924(3) Å), bonds of intermediate length to the phenolic oxygen donors of the pentadentate ligand (Cu(1)–O(2), 1.913(3) Å; Cu(2)–O(3), 1.909(3) Å), longer bonds to the phenyl acetate oxygen donors (Cu(1)–O(4), 1.924(3) Å; Cu(2)–O(5), 1.954(3) Å), and bonds to the imine nitrogen atoms (Cu(1)–N(2), 1.926(3) Å; Cu(2)–N(1), 1.930(3) Å) and the weak out-of-plane interaction between Cu(2) and O(3), 2.523(3) Å. Thus in this complex, one copper atom is four-coordinate and the other is five-coordinate as is indicated by the solid state UV–Vis spectra of this compound (see discussion of UV–Vis spectra (Section 3.3.)).

The two sets of donor atoms form planes from which the copper atoms deviate only slightly (Cu(1), 0.062 Å; Cu(2), 0.078 Å). The dihedral angle between the planes is only 9.2°.

4.2. *Reaction chemistry with phenols and catechols*

An interesting feature of this structure is the presence of a 4-ethylphenol molecule which has a strong hydrogen bond to one of the phenolic oxygen donor atoms of the SalDpl^{3-} ligand (O(6)–O(2), 2.745(4) Å) as well as a weaker hydrogen bond to the adjacent oxygen donor atom from the phenylacetate ion (O(6)–O(4), 3.147(4) Å). This causes a slight lengthening of the Cu(1)–O(2) bond length (1.913(3) Å) compared with the Cu(2)–O(3) bond length (1.909(3) Å). A similar, but greater, effect due to this type of interaction was observed in the 4-nitrophenol adduct of CuSalen [6].

The reaction between the binuclear copper(II) complexes reported in this paper and phenols and catechols produces three different kinds of complexes.

(i) In the absence of a base to deprotonate the phenol or catechol, the phenol does not coordinate to either of the copper atoms but hydrogen bonds to the ligand as shown in the structure of [Cu_2SalDpl(Phenac)(4-Ethylphenol)]. Suitable crystals for the determination of the crystal structure of one of the catechol adducts of [Cu_2SalDpl(Phenac)] could not be grown. The similarity of the spectral and magnetic properties of the phenol and catechol adducts suggests that the catechol molecules in these complexes are also hydrogen bonded to the ligand and are not coordinated to the copper atoms.

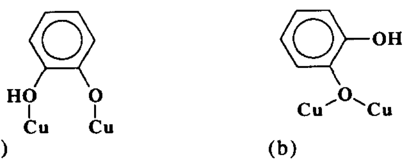


Fig. 11. Possible bridging modes of bonding for a deprotonated catechol ligand.

(ii) In the presence of the base piperidine, using the reaction conditions described in Section 2 of this paper, attempts to make phenol bridged binuclear complexes were unsuccessful. The product obtained from these reactions was always [Cu_2SalDpl(OH)]·nH_2O.

(iii) Using the same reaction conditions with the ligand SalDpl^{3-} and excess catechol, the products obtained always had a ratio of 2:1 for the binuclear copper complex:catechol. No 1:1 products were prepared by this reaction method. Construction of molecular models of these complexes indicates that the 2:1 complexes are less sterically hindered than the 1:1 complexes although molecular models of both types of structure can be made. The 2:1 products may form preferentially because they are less sterically hindered or because they are less soluble than the 1:1 compounds under the reaction conditions used.

A possible structure for these complexes involving a bridging catechol was described in Section 3.4. of this paper (Fig. 10).

(iv) Using the same reaction conditons with the more flexible ligand SalDpe^{3-} and excess catechol, 1:1 complexes were obtained. The stoichiometry of the complexes require that the catechol have a charge of −1. This could be achieved by deprotonation of one of the two phenolic oxygen atoms or partial oxidation of the catechol to the semiquinone. There does not appear to be any infrared evidence for the presence of the semiquinone ligand so it appears that deprotonation occurs at one of the two oxygen atoms. Two possible bridging modes are shown in Fig. 11. There is no infrared evidence for the presence of the free phenolic OH group present in the μ-1,1 bridging mode in Fig. 11(b) so the μ-1,2 bridging mode in Fig. 11(a) would seem the more likely of the two possibilities. This μ-1,2 mode of bonding has been proposed [4] to occur in the tyrosinase reaction cycle.

5. Conclusions

The structure of [Cu_2SalDpl(Phenac)(4-Ethylphenol)] suggests that phenols and catechols can bind to binuclear copper(II) complexes without actually coordinating to either of the copper atoms. With the binuclear complexes used in this work, the use of the base piperidine is needed to deprotonate the catechols so they can bind to the copper atoms. This suggests that, in type III copper proteins such as tyrosinase, the incoming phenol could possibly hydrogen bond to part of the protein chain near the active site before the hydroxylation reaction takes place. Coordination of the phenol to one of the type III copper atoms at the active site would then occur only after deprotonation of the phenol. The ligand SalDpe^{3-} forms good model compounds for the predicted catechol bridged intermediate in the oxidation of catechols by tyrosinase because: (i) the catechol binds to the binuclear complex in the correct 1:1 ratio; (ii) the antiferromagnetic interaction in the binuclear catechol bridged complexes is almost as strong as that in tyrosinase with the complexes being almost diamagnetic at room temperature. A crystal structure of one of these catechol bridged binuclear complexes is needed to help further evaluate the suitability of these complexes as model compounds of the tyrosinase system. Attempts to grow suitable crystals of these complexes have been unsuccessful.

6. Supplementary material

Full tables of bond lengths and angles and of hydrogen coordinates have been deposited with the Cambridge Data Base. Tables of comparisons between observed and calculated structure factors are available.

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