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Characterization and catecholase-mimetic behavior of imidazole adducts of copper(II) valproate. Crystal structure of the 2-methylimidazole adduct

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Abstract

Four mononuclear imidazole adducts of copper(II) valproate have been prepared and characterized with IR, UV–Vis, EPR spectroscopic techniques and fast atom bombardment mass spectrometry. The catecholase-mimetic catalytic activities of the complexes have been determined by monitoring the formation of *o*-quinone from catechol. The catalytic activities of the mononuclear complexes are lower than that of the dinuclear copper(II) valproate. The complexes with 2-methylimidazole and 1,2-dimethylimidazole show slightly lower activities that the imidazole and *N*-methylimidazole complexes. The structure of $Cu(Val)_2(2mIm)_2$ (Val = valproate; 2mIm = 2-methylimidazole) has been determined. The complex crystallizes in the $P2_1/c$ space group with unit cell dimensions of $a = 9.309(1)$, $b = 12.456(2)$, $c = 12.560(2)$ Å, $\beta = 99.84(1)°$, $V = 1435.0(3)$ Å^3, $Z = 2$.

Introduction

Valproic acid (2-propylpentanoic acid) in the form of its sodium salt has a wide spectrum of activity as an anticonvulsant drug [1]. It is well known that copper(II) complexes of anticonvulsant and anti-inflammatory ligands are often more active and desirable drugs than the ligands themselves [2]. Physical studies of copper(II) valproate [3] have shown that it contains dinuclear units with bridging carboxylate ligands similar to other copper(II) carboxylates [4]. The only known adducts of copper(II) valproate are those with pyridine and aniline, which have been shown to be dinuclear complexes of the type $[Cu(O_2CR)_2L]_2$ [3, 5]. The pyridine adduct is unstable, however a X-ray crystal structure analysis has been performed on a crystal sealed in a glass capillary [5].

As part of our research on the interaction of copper(II) carboxylates with imidazoles as models for copper proteins that contain both the imidazole and carboxylate functionalities in the side chain [6], we recently reported the structures of several mononuclear adducts of copper(II) carboxylates with various imidazole ligands [7–12]. The mononuclear complexes of imidazole and *N*-methylimidazole can exist as *trans* bis-adducts and tetrakis-, pentakis- and hexakis-adducts [7, 9, 10, 12, 13]. The adducts of 2-methyl or 1,2-dimethylimidazole can exist as *cis* bis-adducts [8, 9]. The *N*-methylimidazole adduct of copper(II) acetate is dinuclear with two acetate ligands acting as monodentate bridging ligands [14].

Because of the dependence of the structures of copper(II) carboxylates on the electronic property of the carboxylate groups [4a, c], and the electronic and steric properties of added bases [7–10, 15–17], we have used valproic acid and various imidazole derivatives to form copper(II) valproate adducts.

Mononuclear copper(II) carboxylates with imidazoles have been found to have a variety of pharmacological effects [11, 18, 19]. We recently reported the catecholase-mimetic activity of copper(II) aspirinate bis-adducts with benzimidazoles and metronidazoles [11]. These complexes mimic the behavior of various metalloproteins, such as the copper-containing protein tyrosinase, which is found in many plants and animals and whose primary function is to catalyze the oxidation of phenols to *o*-diphenols (cresolase) and *o*-diphenols to *o*-quinones (catechelase) [20]. This article reports the synthesis, spectroscopic characterization and catecholase-mimetic

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activity of four bis-adducts of copper(II) valproate with imidazole and its methyl derivatives. These activities are compared to that of the dinuclear copper(II) valproate. In addition, the X-ray structural characterization of *trans*-bis(2-methylimidazole)bis(valproato)copper(II) is reported.

Experimental

All chemicals were of high purity grade (Aldrich or Sigma Chemical Co.) and were used without further purification. All solvents were anhydrous. Tetrakis-μ-(valproato)dicopper(II), $[Cu_2(Val)]_4$ (**1**) (Val = valproate ion) was prepared according to a published procedure [3, 5] and recrystallized from absolute ethanol.

Bis(imidazole)bis(valproato)copper(II), $[Cu(Val)_2(Im)_2]$ (2)

A solution of 0.199 g (2.92 mmol) of imidazole in 15 ml chloroform was added to 0.50 g (0.71 mmol) of $Cu_2(Val)_4$. The mixture was stirred at about 60 °C for 1 h. The blue solution was filtered and allowed to stand in the refrigerator. The bluish-violet crystals that formed were collected, washed with chloroform and anhydrous diethyl ether, and air dried. *Anal.* Calc. for $C_{22}H_{38}N_4O_4Cu$: C, 54.30; H, 7.82; N, 11.52. Found: C, 54.12; H, 7.76; N, 11.69%.

Bis(N-methylimidazole)bis(valproato)copper(II) · 1.5H_2O, $[Cu(Val)_2(NmIm)_2] \cdot 1.5H_2O$ (3)

A solution of 5 ml of anhydrous *N*-methylimidazole in 5 ml methanol was added to 0.50 g $Cu_2(Val)_4$. The mixture was stirred at room temperature for 1.5 h. The blue solution was filtered and left in the hood to evaporate. The blue crystals that formed were recrystallized from methanol and dried in a desiccator over anhydrous calcium chloride. *Anal.* Calc. for $C_{24}H_{45}N_4O_{5.5}Cu$: C, 53.27; H, 8.32; N, 10.36. Found: C, 53.31; H, 8.31; N, 10.11%.

Bis(2-methylimidazole)bis(valproato)copper(II), $[Cu(Val)_2(2mIm)_2]$ (4)

A solution of 0.24 g (2.92 mmol) of 2-methylimidazole in 25 ml chloroform and 2 ml methanol was added to 0.50 g (0.71 mmol) of $Cu_2(Val)_4$. The mixture was stirred at approximately 60 °C for 1 h. The solution was filtered while hot into anhydrous diethyl ether and stirred until a blue precipitate formed. The blue complex was filtered under reduced pressure, and rapidly changed to purple upon dryness. The product was washed several times with chloroform and anhydrous diethyl ether and air dried. Recrystallization from hot methanol/benzene produced purple crystals suitable for X-ray analysis. *Anal.* Calc. for $C_{24}H_{42}N_4O_4Cu$: C, 56.02; H, 8.17; N, 10.89. Found: C, 55.98; H, 8.12; N, 11.02%.

Bis(1,2-dimethylimidazole)bis(valproato)copper(II) · 0.75H_2O, $[Cu(Val)_2(12dmIm)_2] \cdot 0.75H_2O$ (5)

A solution of 10 ml of 1,2-dimethylimidazole and 3 ml methanol was added to 0.50 g of $Cu_2(Val)_4$. The mixture was stirred at about 60 °C for 0.5 h. The blue solution was filtered into anhydrous diethyl ether and set aside in the hood to evaporate. The blue crystals that formed within one week were collected, washed with anhydrous diethyl ether and dried in a desiccator over anhydrous calcium chloride. *Anal.* Calc. for $C_{26}H_{47.5}N_4O_{4.75}Cu$: C, 56.21; H, 8.56; N, 10.09. Found: C, 56.00; H, 8.54; N, 9.97%.

Physical measurements

Solution room-temperature (298 K) magnetic moments were determined by the Evans method [21] with a Bruker AC 250 MHz NMR spectrometer. Methanol was used as the solvent and TMS as the reference. The effective magnetic moment is related to the reference shift, $\Delta\nu$ (Hz), at any temperature by the expression $\mu_{eff} = 0.0618(\Delta\nu\ T/\nu M)^{1/2}$, where ν is the NMR frequency in MHz and M is the molarity of the paramagnetic substance.

Electronic spectra of methanol solutions were obtained with a Hewlett Packard 8425A diode array spectrophotometer. Nujol mulls sealed between polyethylene sheets were used to obtain IR spectra in the 4000 to 450 cm^{-1} region with a FTS-7 Bio-Rad SPC 3200 Fourier transform infrared spectrometer. Fast atom bombardment mass spectra for the four mononuclear complexes were obtained by dissolving the samples in DMF to which glycerol was then added. The EPR spectra of powdered samples and methanol/toluene solutions at liquid nitrogen temperature were taken with a JEOL Jes-PE-1X spectrometer. Diphenylpicryl hydrazide (DPPH, $g = 2.0036$) was used as the calibrating field marker.

The catecholase-mimetic activities in air were followed spectrophotometrically by monitoring the increase in the *o*-quinone absorbance at 390 nm as a function of time. Methanol solutions of the copper(II) complexes (0.3 ml of 1×10^{-3} M) and 2.0 ml of a methanol solution (0.10 M) of catechol were combined in a 1 cm quartz cell at 298 K and the absorbance changes at 390 nm were recorded.

Crystal structure determination of $[Cu(Val)(2mIm)_2]$ (2mIm = 2-methylimidazole)

Single crystals of **4** were grown from methanol/benzene solution. A bluish-purple plate was selected for X-ray analysis. The crystal was coated with Paratone N, a heavy colorless oil obtained from Exxon Corporation, and attached to the end of a glass fiber. The

TABLE 1. Crystal and data collection parameters for $Cu(Val)_2(2mIm)_2$ (4)

Formula	$C_{24}H_{42}CuN_4O_4$
Formula weight	514.2
Space group	$P2_1/c$
a (Å)	9.309(1)
b (Å)	12.456(2)
c (Å)	12.560(2)
β (°)	99.84(1)
V (Å^3)	1435.0(3)
Z	2
D_{calc} (g/cm^3)	1.190
Crystal size (mm)	0.50×0.50×0.10
μ (cm^{-1})	7.92
Radiation (monochromated incident beam): λ(Mo Kα) (Å)	0.71073
Temperature (K)	155
Scan method	2θ–θ
Diffractometer type	Siemens R3m/V
Data collection, 2θ range (°)	3.5–45
No. unique data; total with $F_o > 4\sigma(F_o)$	1887; 1386
No. parameters refined	151
R[a]	4.79
R_w[b]	5.83
GOF	1.44
Largest and mean Δ/σ	0.001, 0.000
Largest peak (e/Å^3)	0.47

[a]$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{1/2}$, $w = 1/(\sigma^2(F_o) + 0.0009(F_o)^2)$.

TABLE 2. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3) for 4

	x	y	z	U_{eq}[a]
Cu	0	0	0	28(1)
O(1)	1999(3)	−110(3)	836(2)	38(1)
O(2)	998(4)	−1684(3)	1087(3)	45(1)
N(1)	−697(4)	574(3)	1276(3)	30(1)
N(2)	−1039(5)	1551(4)	2654(3)	43(2)
C(1)	865(6)	2210(5)	1629(4)	56(2)
C(2)	−279(5)	1447(4)	1846(4)	36(2)
C(3)	−1991(6)	707(4)	2600(4)	46(2)
C(4)	−1779(5)	124(5)	1747(4)	39(2)
C(5)	2018(6)	−1065(5)	1265(4)	41(2)
C(6)	3426(6)	−1324(5)	2041(4)	57(2)
C(7)	3594(6)	−614(6)	3011(4)	60(2)
C(8)	2318(8)	−576(7)	3608(5)	82(3)
C(9)	2433(9)	156(8)	4546(5)	111(4)
C(10)	4709(6)	−1361(5)	1462(5)	55(2)
C(11)	4565(7)	−2054(6)	462(6)	74(3)
C(12)	5844(8)	−2054(6)	−112(7)	88(3)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

fiber was mounted on a goniometer head and placed in a N_2 steam (155 K) on the goniometer. Unit cell dimensions were determined from least-squares refinement of 49 randomly selected high angle ($24 < 2\theta < 45°$) reflections. These reflections were used to determine an orientation matrix and the symmetry

TABLE 3. Bond lengths (Å) and bond angles for (°) for 4

Cu–O(1)	1.979(3)	Cu–N(1)	1.964(4)
O(1)–C(5)	1.305(7)	O(2)–C(5)	1.214(7)
O(1)–Cu–N(1)	90.2(1)	Cu–O(1)–C(5)	103.1(3)
O(1)–C(5)–O(2)	123.2(4)	O(1)–C(5)–C(6)	113.9(5)
O(2)–C(5)–C(6)	122.9(5)		

TABLE 4. Magnetic moments and electronic and IR spectral data for Cu(II) complexes

Compound	μ_{eff} (BM) (298 K)	λ_{max} (nm) (ϵ)[a]	$\nu_{asym}(CO_2)$ (cm^{-1})	$\nu_{sym}(CO_2)$ (cm^{-1})
2	1.88	686 (75)	1575(br)[b]	1412
3	1.89	684 (66)	1583(br)	1398
4	1.86	675 (80)	1581	1417
5	1.87	686 (83)	1565(br)	1404

[a]ϵ in units of dm^3 mol^{-1} cm^{-1}. [b]br is broad band overlaps with imidazole bands.

class. Data were collected on a Siemens R3mV diffractometer between 3.5 and 45° in 2θ. The data were corrected for Lorentz and polarization effects but not for absorption. The absorption coefficient was 7.9 cm^{-1}. The structure was solved by heavy-atom methods and successive Fourier syntheses [22]. During the latter refinements, the hydrogen atoms were included at their calculated positions and were not refined but were allowed to ride along with their bonded atoms. The final least-squares cycle of full-matrix refinement gave $R = 0.0479$ and $R_w = 0.0583$. Other crystallographic and procedural data are given in Table 1. Atomic positional parameters are found in Table 2 and selected bond distances and angles are presented in Table 3.

Results and discussion

Magnetic and spectroscopic results

The effective magnetic moments and electronic and IR spectral data are summarized in Table 4. The room temperature (298 K) magnetic moments for complexes **2–5** are consistent with the presence of one unpaired electron in a mononuclear copper(II) complex. The electronic spectra of the complexes in methanol solution exhibit one broad absorption band in the 675–686 nm region (Table 4). This band is assigned to the copper(II) d–d transition. The spectra lack the charge transfer band near 370 nm that is characteristic of dinuclear copper(II) carboxylate adducts [3, 4]. The position of the d–d transitions and the magnitude of their molar absorptivities are in the range expected for mononuclear copper(II) complexes that contain a $CuN_2O_2...O_2$ chromophore [4c, 7–10].

The assignments of IR frequencies for the antisymmetric stretch, $\nu_{asym}(CO_2)$, and the symmetric stretch,

TABLE 5. ESR and kinetic data for the oxidation of catechol by Cu(II) complexes

Compound	State	$g_\perp$	$g_\parallel$	$A_\parallel$Cu ($\times 10^4$ cm^{-1})	$A_\perp$N ($\times 10^4$ cm^{-1})	Activity[a]
1	solid[b]	2.016	2.341			0.335
2	solid	2.075	2.189			0.084
	[c]	2.054	2.271	164	15	
3	solid	2.056	2.247			0.088
	[c]	2.062	2.273	167	14	
4	solid	$g_x = 2.060$ $g_y = 2.084$	2.202			0.040
	[c]	2.056	2.291	155	13.5	
5	solid	[d]	[d]			0.055
	[c]	[e]	2.28	163	14	

[a]The activity is reported as micromoles of *o*-quinone produced per mg catalyst per min. [b]The g values are taken from ref. 3. [c]Frozen solution. [d]Only one peak is observed with $g = 2.094$. [e]The structure observed in the $g_\perp$ region is interpreted as the overlap of ^{14}N hyperfine structure of g_x and g_y components; however, the possibility of Cu hyperfine coupling in the perpendicular g components cannot be completely ruled out.

$\nu_{sym}(CO_2)$, of the valproate group are given in Table 4. Broad bands assigned to $\nu_{asym}(CO_2)$ occur between 1565 and 1583 cm^{-1}, and bands for $\nu_{sym}(CO_2)$ between 1398 and 1417 cm^{-1}. The band positions and the separation $\Delta\nu$ ($\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$), between 161 and 185 cm^{-1}, when compared with those of sodium valproate ($\nu_{asym}(CO_2)$, 1570; $\nu_{sym}(CO_2)$, 1417; $\Delta\nu$, 153 cm^{-1}) are in the range expected for carboxylate groups that act as unsymmetrical bidentate ligands [8–11, 23]. These parameters are comparable to those reported for mononuclear copper(II) carboxylate complexes that contain $CuN_2O_2...O_2$ chromophore [8–12, 24]. These coordination features are verified by the solid state structure for $Cu(Val)_2(2mIm)_2$ (**4**).

Fast atom bombardment (FAB) mass spectrometry was used to help characterize complexes **2–5**. Initial attempts to obtain FAB spectra in the standard matrices glycerol and thioglycerol were unsuccessful, apparently because of lack of solubility. Dissolving the samples in DMF and adding glycerol subsequently produced spectra of the samples [25]. Previous FAB studies on copper(II) complexes did not produce spectra directly, but revealed the existence of ions formed from reduction of the Cu(II) to Cu(I). The parent peaks for complexes **2–5** occur at *m/z* for CuL_2^+ cations (where L is imidazole or a methyl derivative) with relative intensity between 90 and 100%. It results from the loss of two valproate anions and the reduction of Cu(II) to Cu(I) [25]. The second most intense peaks in the spectra occur at *m/z* for the CuL^+ cation with relative intensity between 25 and 45%. FAB mass spectra showing similar fragments have been obtained for bis(imidazole)copper(I) complexes [25]. The spectral data thus suggest that all four mononuclear complexes have the same stoichiometry, $Cu(Val)_2(L)_2$.

The EPR parameters, g and A, for the frozen solution and solid-state spectra of **2–5** are given in Table 5. A representative frozen solution EPR spectrum is that of **5** shown in Fig. 1(a). The frozen solution EPR spectra exhibit resolved structure with $g_\parallel > g_\perp (g_x, g_y)$ and are consistent with a tetragonally elongated structure [26]. While the $g_\parallel$ regions exhibit typical Cu hyperfine coupling, the $g_\perp$ regions exhibit structure that is ascribed to ^{14}N superhyperfine interactions attributable to the presence of two nitrogen atoms in the copper(II) ion plane. Similar interactions and splittings are typical for the CuN_xO_{4-x} chromophore ($x = 1$–4). The number of lines in the $g_\perp$ region of **5** might result from the loss of equivalence of g_x and g_y due to anisotropy such that both components show ^{14}N splitting. EPR spectral parameters for **2–5** are comparable to those previously reported for complexes that contain essentially the CuN_2O_2 chromophore in a *trans* or *cis* square-planar arrangement, including those reported for mononuclear bis-adducts of copper(II) carboxylates with imidazoles [4c, 8–11, 18, 19, 24]. In complexes for which structural data are available, the copper(II) atom is bonded in a *trans* or *cis* arrangement to two ligand nitrogen atoms and one oxygen atom from each of the two carboxylate ligands. The second oxygen atom of each carboxylate ligand is weakly bonded in a pseudo axial arrangement [8–10, 12, 13, 25].

The solid-state EPR spectra of **2**, **3** and **4** are anisotropic and contain $g_\parallel$ and $g_\perp$ components. Two of the four copper(II) hyperfine components in the $g_\parallel$ region for complex **3** are partially resolved. Comparable spectra and spectral parameters are exhibited by the bis-adduct of tetrakis(ferrocenecarboxylato)copper(II) with *N*-methylimidazole [9]. We have determined by single crystal X-ray structure analysis that this adduct contains the CuN_2O_2 chromophore in a *trans* square-

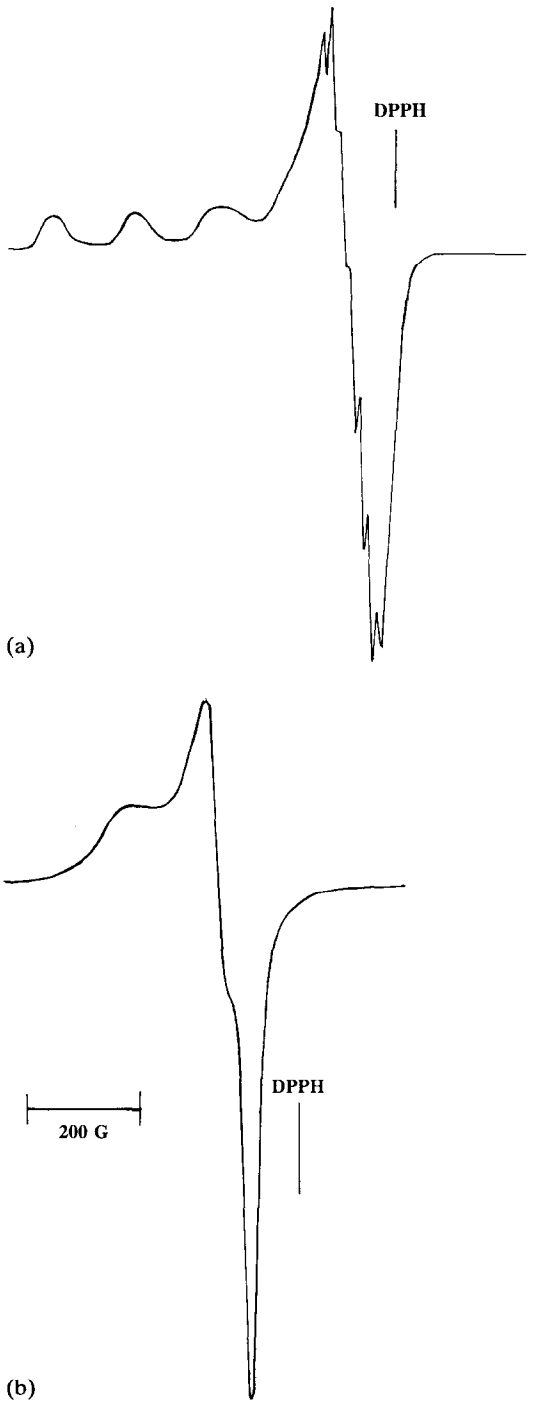

Fig. 1. (a) Frozen-solution EPR spectrum of **5**. (b) Solid state EPR of **4**.

planar arrangement [9]. The $g_\perp$ region for **4** is partially resolved into its x and y components as shown in Fig. 1(b). This is consistent with the CuN_2O_2 chromophore for which a slight deviation from true square-planar environment occurs.

The solid-state EPR spectrum of **5** contains an asymmetric signal centered near 3200 G. Similar spectra are exhibited by bis-adducts of copper(II) acetate and copper(II) ferrocenecarboxylate with 1,2-dimethylimidazole [8, 9]. A single crystal X-ray structural analysis indicates that these adducts contain the CuN_2O_2 chromophore in a *cis* square-planar arrangement [8, 9]. The lack of copper(II) hyperfine coupling in these complexes is likely due to dipole–dipole interactions between copper(II) atoms of neighboring molecules. Although we were unable to obtain X-ray data for **5** of sufficient quality for publication, a preliminary structure clearly indicates that in the solid state **5** contains the CuN_2O_2 chromophore in a *cis* square-planar arrangement, similar to other bis-adducts of the aforementioned copper(II) acetate and ferrocenecarboxylate with 1,2-dimethylimidazole [8, 9]. The spectral data strongly suggest the presence of the CuN_2O_2 (or $CuN_2O_2...O_2$) chromophore in *trans* or *cis* square-planar arrangements for **2–5**. In the case of **4** this is supported by a X-ray structure determination (*vida infra*).

Catecholase-mimetic activity

The rates of the catalyzed oxidation of catechol to *o*-quinone by **2–5** were obtained and compared to that of the dinuclear complex **1**. The oxidation was monitored by recording the change in absorbance of *o*-quinone at 390 nm over the first 30 min of the reaction. The activities of the complexes were determined as micromoles of *o*-quinone produced per mg of catalyst per minute. These values are given in Table 5. Although *o*-quinone is produced for all complexes, the rate at which it is produced varies significantly from dinuclear to mononuclear catalysts. The rate at which *o*-quinone is produced is also dependent on the type of imidazole ligand present in the mononuclear complexes.

Small molecular weight dinuclear and mononuclear copper(II) complexes have been studied as models for copper oxidase enzymes, such as the copper-containing protein tyrosinase [11, 27–29]. In tyrosinase and in synthetic copper(II) dinuclear models, it is believed that two proximate metal atoms are needed to bond to the two hydroxyl oxygen atoms of catechols in the oxidation to *o*-quinones [27–29]. This is consistent with the relatively high catalytic activity of dinuclear complexes such as **1** compared to mononuclear complexes such as **2–5** (Fig. 2, Table 5). In non-planar mononuclear copper(II) models, it has been proposed that the two copper(II) atoms must be located at a distance of less than 5 Å for bonding to the hydroxyl groups of the catechols, a mode which should facilitate electron transfer to dioxygen [27, 29a]. The catecholase-mimetic activities of the imidazole adduct **2** and the *N*-methylimidazole adduct **3** are higher than those of 2-methylimidazole (**4**) and the 1,2-dimethylimidazole adduct (**5**) (Table 5). This may be due to steric hindrance caused by the proximity of the methyl group to the

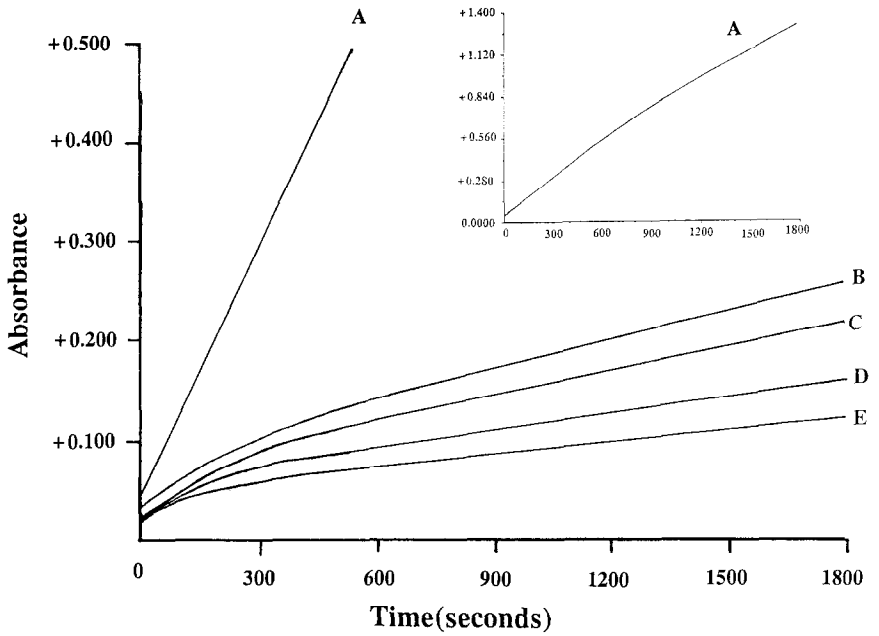

Fig. 2. Absorbance changes at 690 nm during the catalytic oxidation of catechol to *o*-quinone by **1** (A), **3** (B), **2** (C), **5** (D) and **4** (E). Insert shows changes over the entire 30 min period for **1**.

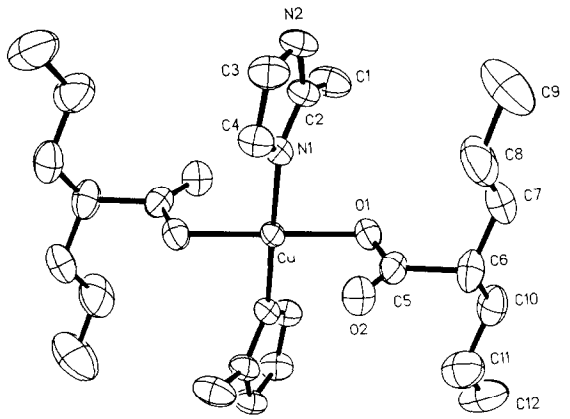

Fig. 3. Structure of **4**.

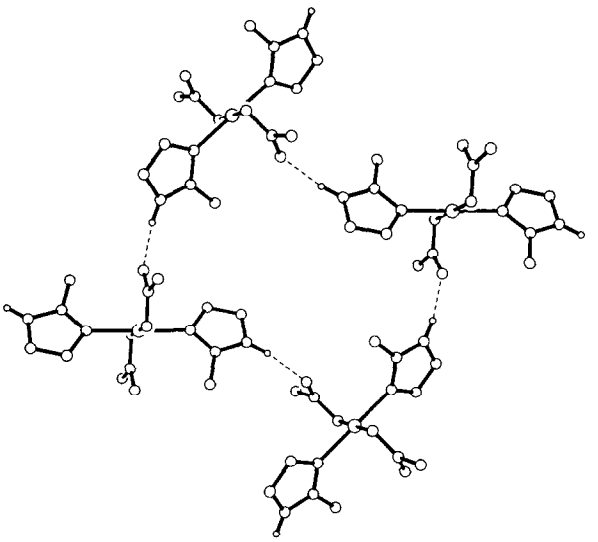

Fig. 4. Partial solid-state hydrogen bonding network for **4**.

nitrogen donor atom in **4** and **5**. The presence of methyl groups could render the approach of catechol to the Cu(II) sites more difficult in these two adducts when compared to the imidazole and *N*-methylimidazole adducts. These results are consistent with our previous studies which revealed that the catecholase-mimetic activity of the mononuclear copper(II) aspirinate adduct with benzimidazole is higher than that of 2-methylbenzimidazole and the metronidazole (1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole) adduct [11].

Molecular structure

The structure of **4** is shown in Fig. 3. The molecule sits on a crystallographic inversion center with the Cu atom located on the special position (0,0,0); thus the asymmetric unit consists of one-half of one molecule. The Cu atom occupies essentially a *trans* square-planar environment with the two imidazole nitrogen atoms at 1.964(4) Å and two carboxylate oxygen atoms at 1.979(3) Å. The remote carboxylate oxygen atoms are 2.587 Å from the Cu atom allowing for weak interactions at best. The least-squares plane of the imidazole rings forms a dihedral angle of 121.1° with the least-squares plane of the Cu atom and the donor atoms that form the square-planar environment. The remote carboxylate oxygen atoms are involved in hydrogen bonding inter-

actions with the N–H functions of the 2-methylimidazole ligands of neighboring molecules. Using a N–H distance of 0.900 Å to locate the hydrogen atoms in their calculated position, the O(2)···H distance is 1.819 Å and the donor–acceptor separation O(2)···N is 2.705 Å. A partial hydrogen bonding network is illustrated in Fig. 4.

Supplementary material

Complete tables of bond lengths and angles, anisotropic thermal parameters, and observed and calculated structure factors are available from the authors on request.

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