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Dinuclear copper(II) complexes: Solvent dependent catecholase activity

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ABSTRACT

Four new dicopper(II) complexes of phenol based compartmental ligands, namely $[Cu_2(L^1H)_2(H_2O)_2(NO_3)_2](NO_3)_2$ (**1**), $[Cu_2(L^2)(OH)(H_2O)(NO_3)](NO_3)$ (**2**), $[Cu_2(L^3)_2(H_2O)(NO_3)](NO_3)$ (**3**) and $[Cu_2(L^4)(H_2O)_2(NO_3)](NO_3)_2$ (**4**) [where L^1 = 2-formyl-4-methyl-6-(4-(aminomethyl)-piperidine)iminomethyl-phenolato, L^2 = 2,6-bis(2-amino-2-methyl-1-propanol)iminomethyl-4-methyl-phenolato, L^3 = 2-formyl-4-methyl- 6-(benzylamine)iminomethyl-phenolato and L^4 = 2,6-bis(2-aminoethylpyridine)iminomethyl-4-methyl-phenolato] have been synthesized and structurally characterized. The single crystal X-ray analyses reveal that all four complexes are dinuclear in nature; complexes **2** and **4** comprise of one respective ligand, whereas **1** and **3** are contain two respective ligands, and the Cu–Cu separation in each case is *ca.* 3.0 Å. All four complexes are soluble in dichloromethane (DCM), methanol, acetonitrile (ACN), dimethylsulfoxide (DMSO), water–methanol (50:50, v/v), and this property has been exploited to access the solvent effect on the catecholase activity of the complexes towards the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ. A UV–Vis spectral study in the different solvents, followed by a kinetic investigation, suggests that the change in spectral behavior follows a similar trend, being dependent on the coordinating ability of the solvent, irrespective of the complex used. The commonly known physical parameters of the solvents, like the dielectric constant, dipole moment, polarity, etc., do not seem to be a key factor in controlling the catecholase activity. However, protic solvents are observed to be a better choice than aprotic solvents for the oxidation of 3,5-DTBC.

1. Introduction

Synthetic analogs of catechol oxidase have been studied in great depth in recent years in order to understand the structure–function relationship and to find out the different external factors that affect the activity of these systems [1–20]. It is presently well established that internal factors, which have a profound effect on the catalytic activities of model compounds, are (i) the Cu–Cu distance: the best activity can be achieved when the separation is ~3 Å; (ii) the flexibility of the coordinating ligands: the greater the flexibility, the higher the activity; (iii) the coordination environment of the copper centers: coordination unsaturation or the presence of highly labile ligands like water molecules enhance the activity. At the same time, the presence of a positive charge center close to the active site may improve the activity. Amongst the external factors, the most crucial are (i) the nature of the model substrate; presence of bulky electron donating group(s) make the substrate easy to get oxidized, (ii) the pH of the medium; the higher the pH greater the activity and (iii) the nature of the solvent. Although most of the external factors have been studied in great detail, interestingly a great scarceness is observed as far as investigations on the effect of solvent on the catecholase activity of model compounds are concerned. In order to get a better comprehension of the solvent effect, a prerequisite should be the solubility of complexes in a wide choice of solvents, a result sometimes difficult to achieve. However, fortunately we have obtained four phenol based compartmental ligand (Scheme 1) complexes of dicopper(II), namely $[Cu_2(L^1H)_2(H_2O)_2(NO_3)_2](NO_3)_2$ (**1**), $[Cu_2(L^2)(OH)(H_2O)(NO_3)](NO_3)$ (**2**), $[Cu_2(L^3)_2(H_2O)(NO_3)](NO_3)$ (**3**) and $[Cu_2(L^4)(H_2O)_2(NO_3)](NO_3)_2$ (**4**) [where L^1 = 2-formyl-4-methyl-6-(4-(aminomethyl)-piperidine)iminomethyl-phenolato, L^2 = 2,6-bis(2-amino-2-methyl-1-propanol)iminomethyl-4-methyl-phenolato, L^3 = 2-formyl-4-methyl-6-(benzylamine)iminomethyl-phenolato and L^4=2,6-bis(2-aminoethylpyridine)iminomethyl-4-methyl-phenolato], which are soluble in several solvent systems, namely dichloromethane (DCM), methanol, acetonitrile (I), dimethylsulfoxide (DMSO) and water–methanol (50:50, v/v), and we have taken advantage of this chance to shed some light on that untouched corner of catecholase activity, i.e. the solvent effect on catecholase

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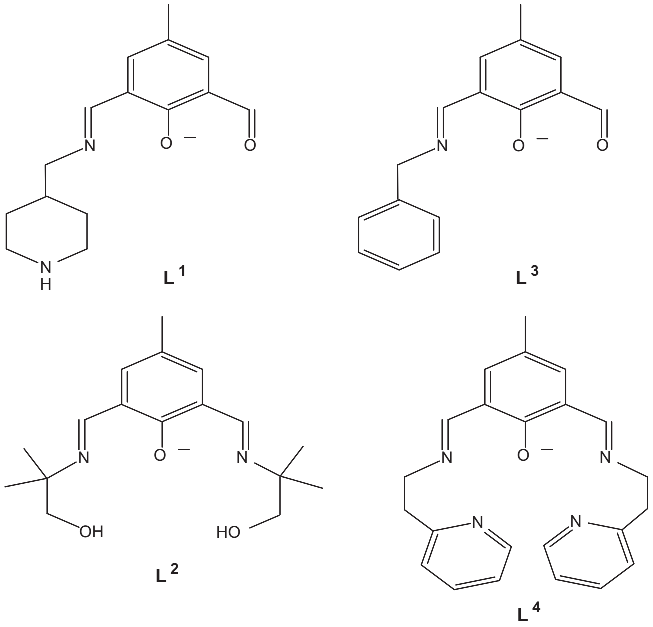

Scheme 1. Chemical drawing of the four ligand systems.

activity, namely the solvent effect on the activity of this enzyme using 3,5-di-*tert*-butylcatechol (3,5-DTBC) as a model substrate.

2. Experimental

2.1. Starting materials

All materials were obtained from commercial sources and used as purchased. Solvents were dried according to standard procedures and distilled prior to use. 2,6-diformyl-4-methylphenol was prepared according to the literature method [21]. 4-(Aminomethyl)piperidine, 2-amino-2-methyl-1-propanol, 2-(2-aminoethyl)pyridine and benzylamine were purchased from Aldrich Chemical Company and used as received. All other chemicals used were of AR grade.

2.2. Methods and instrumentation

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Copper was estimated gravimetrically with α-benzoin oxime. Infrared spectra (4000–400 cm^{-1}) were recorded at 27 °C using a Shimadzu FTIR-8400S, using KBr pellets. Electronic spectra (800–200 nm) were obtained at 27 °C using a Hitachi U-3501 and using acetonitrile, methanol, dichloromethane, dimethylsulfoxide and methanol–water (50:50, v/v) as the media, as well as references.

2.3. X-ray data collection and crystal structure determinations

Diffraction data for all the structures reported were obtained at room temperature on a Nonius DIP-1030H system ($\lambda = 0.71073$ Å). Cell refinement, indexing and scaling of the data sets were carried out using DENZO and SCALEPACK programs [22]. All the structures were solved by direct methods and subsequent Fourier analyses [23] and refined by the full-matrix least-squares method based on F^2 for all observed reflections [23]. The crystal structure analysis revealed the phenyl rings of **3** manifest high thermal motion and one of these was refined as a rigid hexagon. In **1**, the oxygen atoms of the coordinated nitrate anion were found to be disordered over two positions (each with an occupancy of 0.50, isotropically refined). Finally a lattice water molecule was detected on the ΔF map relating to compounds **2** and **4**. All hydrogen atoms were placed at geometrically calculated positions, except those of water molecules and of hydroxyl anions, where the O–H distances were constrained to 0.85 and 0.80 Å, respectively. All the calculations were performed using the WinGX System, Ver. 1.80.05 [24]. Crystallographic data and experimental details are reported in Table 1.

Table 1
Crystallographic data and details of structure refinements for complexes **1**–**4**.

	1	**2**·H_2O	**3**	**4**·H_2O
Empirical formula	$C_{30}H_{44}Cu_2N_8O_{18}$	$C_{17}H_{30}Cu_2N_4O_{12}$	$C_{32}H_{30}Cu_2N_4O_{11}$	$C_{23}H_{29}Cu_2N_7O_{13}$
Formula weight	931.81	609.53	773.68	738.61
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$I2/a$	$P2_1/c$
a (Å)	13.936(3)	7.101(3)	14.341(4)	10.184(3)
b (Å)	10.017(3)	12.420(3)	27.624(5)	35.631(4)
c (Å)	15.317(3)	14.357(4)	16.515(4)	8.026(2)
α (°)		100.20(3)		
β (°)	115.85(2)	96.17(2)	94.76(3)	97.25(2)
γ (°)		92.62(2)		
Volume ($Å^3$)	1924.3(8)	1236.2(7)	6520(3)	2889.1(12)
Z	2	2	8	4
D_{calc} ($g\ cm^{-3}$)	1.608	1.637	1.576	1.698
μ Mo Kα (mm^{-1})	1.193	1.786	1.372	1.551
$F(000)$	964	628	3168	1512
θ_{max} (°)	27.10	28.70	24.10	23.24
Reflections collected	15617	15303	34525	33858
Unique reflections	4030	5868	4989	3263
R_{int}	0.0352	0.0278	0.0530	0.0750
Observed $I > 2\sigma(I)$	2512	4586	1927	1622
Parameters	265	331	439	424
Goodness of fit (F^2)	0.952	1.035	0.803	0.837
R_1 ($I > 2\sigma(I)$)[a]	0.0579	0.0447	0.0597	0.0459
wR_2[a]	0.1649	0.1303	0.1546	0.1038
$\Delta\rho$ ($e/Å^3$)[b]	0.641, −0.421	0.692, −0.398	0.626, −0.351	0.561, −0.360

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[b] Residuals close to the metal center.