Transition Metal Chemistry (2006) 31:1–12
DOI 10.1007/s11243-005-6249-7
© Springer 2006

Mixed-ligand copper(II) complexes: Investigation of their spectroscopic, catalysis, antimicrobial and potentiometric properties

Mehmet Tümer*, Nihal Deligönül, Ayşegül Gölcü, Eyüp Akgün and Mustafa Dolaz
Department of Chemistry, Faculty of Science and Arts, University of Kahramanmaraş Sütçü Imam, Kahramanmaraş, Turkey

Havva Demirelli
Department of Chemistry, Faculty of Education, Gazi University, Ankara, Turkey

Metin Dığrak
Department of Biology, Faculty of Science and Arts, University of Kahramanmaraş Sütçü Imam, Kahramanmaraş, Turkey

Received 7 April 2005; accepted 22 June 2005

Abstract

Schiff base ligands HL^1–HL^6 have been prepared from the reaction of 2,6-diformyl-4-*t*-butylphenol and 2,6-diformyl-4-methylphenol with various aromatic amines in ethanolic solution. The Schiff base ligands 2,2′-dipyridine (dp) mixed-ligand Cu^{II} complexes have been obtained. Mixed-ligand Cu^{II} complexes containing the dp ligand have ionic nature and they conduct the electricity in solution media. The complexes have been obtained in two different forms: one of them is $[Cu_2(L^n)Cl_3]$ (n: 1, 2, 3, 4, 5 and 6) and other complexes have the general formula $[Cu_2(L^n)(dp)_2]3Cl$. Ligands and their complexes have been characterized by elemental analyses, FT-IR, electronic spectra, molar conductance, $^1H(^{13}C)$-n.m.r. and mass spectral data. Their stoichiometric protonation constants have been determined potentiometrically in dioxan using a combined pH electrode at 25 °C, under a nitrogen atmosphere. For the calculation of the protonation constants, PKAS computer programme has been used. The effects of the substituents on the protonation constants and the additivities of these effects are discussed. The antimicrobial activity studies of the ligands and their complexes have been studied against the *Bacillus megaterium*, *Micrococcus luteus*, *Corynebavterium xenosis*, *Enterococcuc faecalis*, bacteria and *Saccoramyces cerevisia*, yeast. The catalytic properties of the complexes have been studied on the ascorbic acid, catechol and 2,6-di-*t*-butylphenol substrates. Thermal behaviour of the complexes has been studied by thermal techniques.

Introduction

The catecholase activity of copper co-ordination compounds with different structural parameters has been investigated to some extent [1]. In these studies mono- or multi-nuclear complexes have been employed and the properties of the chelating ligands with respect to architecture, number and nature of the donor atoms have been varied. Nishida and co-workers [2] have found that square-planar mononuclear copper(II) complexes exhibit only little catalytic activity while non-planar mononuclear copper(II) complexes show a high catalytic activity.

Dinuclear complexes also catalyse the oxidation process if the Cu···Cu distance is less than 5 Å. A steric match between substrate and complex is believed to be the determining factor: two metal centres have to be located in close proximity to facilitate binding of the two hydroxyl oxygen atoms of catechol prior to the electron transfer [2]. This view is supported by the observation that dinuclear copper complexes are generally more reactive towards the oxidation of catechols than are corresponding mononuclear species [3, 4]. But so far only one crystal structure of a catalytically active dinuclear copper(II) complex with a co-ordinating catecholato ligand has been reported [5]. No direct correlation between the rates of reaction and the redox potentials of complexes has been determined. Malachowski *et al.* [6] have pointed out that a window of redox potentials for effective catalysis exists with a balance between ease of reduction by the substrate and subsequent reoxidation by molecular oxygen. Although some general correlations of structure-reactivity patterns have been found, the exploration of the oxidation chemistry of structurally well-characterised copper complexes is still needed to fully understand the parameters affecting their catecholase activity.

* Author for correspondence: E-mail: mtumer@ksu.edu.tr

The oxidation of organic substrates with molecular oxygen under mild conditions is of great interest for industrial and synthetic processes both from an economical and environmental point of view [7]. Although the reaction of organic compounds with dioxygen is thermodynamically favoured, it is kinetically hindered due to the triplet ground state of O_2. The synthesis and investigation of functional model complexes for metalloenzymes with oxidase or oxygenase activity is therefore of great promise for the development of new and efficient catalysts for oxidation reactions. The catechol oxidases (EC 1.10.3.1) are type 3 copper enzymes containing a dinuclear copper centre [8]. Well-known representatives of these type 3 copper proteins are hemocyanin [9, 10], the dioxygen carrier for arthropods and mollusks, and tyrosinase [11]. Catechol oxidase belongs, like tyrosinase, to the polyphenol oxidases which oxidize phenolic compounds to the corresponding quinones in the presence of oxygen. Whereas tyrosinase (EC 1.14.18.1) catalyzes the hydroxylation of tyrosine to dopa (cresolase activity) and the oxidation of dopa to dopaquinone (catecholase activity) with electron transfer to dioxygen, catechol oxidase exclusively catalyzes the oxidation of catechols to quinones without acting on tyrosine [12]. This reaction is of great importance in medical diagnosis for the determination of the hormonally active catecholamines adrenaline, noradrenaline and dopa [13]. Because of Schiff base diverse uses in science, the protonation constants of such compounds are of interest. Although there is a number of publications on the determination of the protonation constants of the various Schiff bases in solvent or solvent mixtures [14], a literature survey reveals that the protonation constant of Schiff bases prepared from substituted *t*-butyl phenol and 4-methylphenol have not been determined systematically in dioxan solution.

In this study, we synthesized tridentate Schiff base ligands HL^1–HL^6 and their mixed-ligand copper(II) complexes. The protonation constants, catalysis, thermal, antimicrobial activity and spectroscopic properties of the ligands and their Cu^{II} complexes are reported.

Experimental

Materials

All solvents were obtained commercially and were used without further purification. 2,6-di-*t*-butylphenol, catechol, ascorbic acid, *p*-toluidine, 4-bromoaniline, 4-hydroxyaniline, *p*-cresol and 4-*t*-butylphenol were purchased from Fluka. 4-Methyl-2,6-di-formylphenol and 4-*t*-butyl-2,6-di-formylphenol were synthesized according to the literature method [15].

Physical measurements

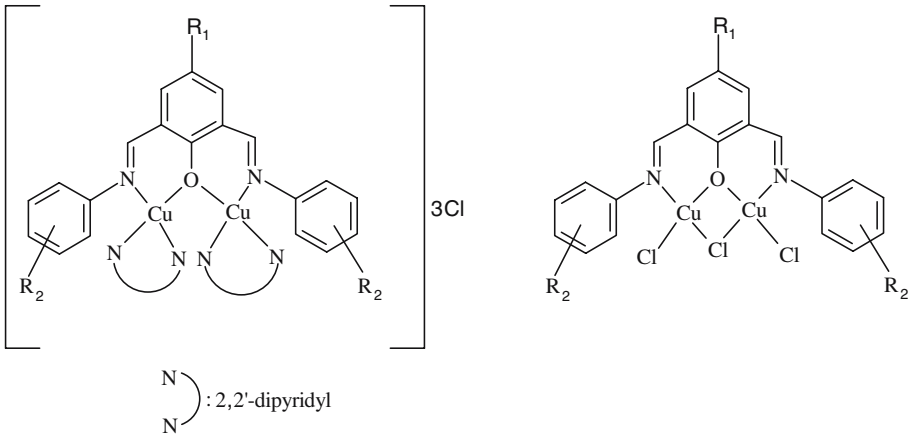
Elemental analyses (C, H, N) were performed using a LECO CHNS 932 (TUBITAK) elemental analyser. I.r. spectra were obtained using KBr discs (4000–400 cm^{-1}) on a Shimadzu 8300 FT-IR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained on a Shimadzu UV-160 A spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of the Schiff base ligands and their transition metal complexes were determined in MeOH ($\sim 10^{-3}$ M) at room temperature using a Jenway Model 4070 conductivity meter. Mass spectra of the ligands were recorded on a VG ZabSpec GC-MS spectrophotometer (TUBITAK) with fast atom bombardment. ^1H and ^{13}C n.m.r. spectra were recorded on a Varian XL-200 instrument. TMS was used as internal standard and deuteriated DMSO as solvent. The metal and chloride contents of the complexes were determined gravimetrically according to the known procedure [16]. Catalysis experiments were monitored on a Shimadzu 160-A UV–vis spectrophotometer with a data station. Experiments were carried out using MeOH as solvent. In a generalised procedure a MeOH solution of 2,6-di-*t*-butylphenol (0.05 cm^3) and the homo- and mixed-ligand Cu^{II} complexes in a 50 cm^3 standard flask were kept under N_2. The compound 2,6-di-*t*-butylphenol (DTBP) was oxidized by aerial oxygen quantitatively to the 3,3′-5,5′-tetra-*t*-butyl-4,4′-diphenoquinone (TTBD) by using the mixed-ligand binuclear complexes Cu^{II} as a catalyst. The change in the concentration of product 3,3′-5,5′-tetra-*t*-butyl-4,4′-diphenoquinone was monitored by optical spectroscopy. For the catalytic activity of the binuclear complexes, a similar procedure was adopted for reactions with ascorbic acid and catechol, the d–d band being monitored. The thermal analyses studies of the complexes were performed on a Perkin Elmer Pyris Diamond DTA/TG Thermal System under nitrogen atmosphere at a heating rate of 10 °C/min.

Preparation of the ligands

All ligands were prepared by a similar method. Solutions of aldehydes (0.01 mol, in 20 cm^3 EtOH) and amine derivatives (0.02 mol, in 20 cm^3 EtOH) were mixed together and refluxed for *ca.* 1 h on a water bath. The precipitated product was filtered and washed with cold EtOH (Figure 1). The ligands were recrystallized from $CHCl_3$/EtOH (1:3 by vol) and dried in a vacuum desiccator over P_2O_5. The purity was checked by elemental analyses and melting point determination.

Preparation of the complexes $[Cu_2(L^n)Cl_3]$

The complexes were prepared by similar methods. A solution of the metal salt (2 mmol) in absolute MeOH



R_1: CH_3, R_2: CH_3 (HL^1); R_1: t-Bu, R_2: CH_3 (HL^2); R_1: CH_3, R_2: Br (HL^3); R_1: t-Bu, R_2: Br (HL^4); R_1: CH_3, R_2: OH (HL^5); R_1: t-Bu, R_2: OH (HL^6)

Fig. 1. General formula of the Schiff Bases with their $[Cu_2(L^x)Cl_3]$ and $[Cu_2(L^x)dp_2]3Cl$ complexes.

(25 cm^3) was added to a solution of the HL^1-HL^6 ligands (1 mmol) in absolute MeOH (20 cm^3) and the mixture was boiled under reflux for 6–7 h. At the end of the reaction, determined by t.l.c., the precipitate was filtered off, washed with distilled H_2O and then EtOH, and dried *in vacuo*.

Preparation of the mixed-ligand complexes $[Cu_2(L^n)(dp)_2]3Cl$

The complexes $[Cu_2(L^n)(dp)_2]3Cl$ were prepared by similar methods. To a solution of the complexes $[Cu_2(L^n)Cl_3]$ (1 mmol) in absolute MeOH (20 cm^3) was added a solution of 2,2′-bipyridine (2 mmol) in MeOH (10 cm^3) and the reaction mixture was boiled under reflux for 6–7 h. The end of the reaction was determined by t.l.c., the precipitate was filtered off, washed with EtOH and MeOH, and dried *in vacuo*.

*Catalytic oxidation of 2,6-di-t-*butylphenol

In a CH_2Cl_2/MeOH solvent mixture (1:1, 50 cm^3), the complexes $[Cu_2(L^n)(dp)_2]3Cl$ (n: 1, 2, 3, 4, 5 and 6) were dissolved. To it 2,6-di-*t*-butylphenol was added and the solution was stirred for 48 h. It was then filtered and the filtrate was evaporated to dryness. 5 cm^3 of MeOH were added to dissolve the excess 2,6-di-*t*-butylphenol. For measuring the progress of the reaction, 50 cm^3 from the aliquot was passed through an Amberlyst cationic ion-exchanger and washed with 10 cm^3 (2 × 5) CH_2Cl_2. The change in the concentration of product 3,3′-5,5′-tetra-*t*-butyl-4,4′-diphenoquinone, was monitored by optical spectroscopy.

Catecholase activity study

The reaction of complexes $[Cu_2(L^n)(dp)_2]3Cl$ with catechol was monitored as follows: 2 cm^3 of a 10^{-4} mol dm^{-3} solution of complex in MeOH were treated with 0.1 cm^3 of a 0.1 mol dm^{-3} solution of catechol in MeOH. The UV/VIS spectra of the original solution, of the solution directly after the addition and after 5, 10, 15 and 20 min were recorded and corrected for volume changes.

Preparation of microorganism cultures

The growth inhibitory activity of the chemical matter was tested against thirteen bacteria [*Corynebacterium xerosis* UC 9165, *Bacillus brevis* NRS, *Bacillus megaterium* DSM 32, *Bacillus cereus* EU, *Mycobacterium smegmatis* CCM 2067, *Staphylococcus aureus* Cowan 1, *Pseudomonas aeruginosa* ATCC 27853, *Klebsiella pneumoniae* FMC 5, *Enterococcus faecalis* ATTC 15753, *Micrococcus luteus* LA 2971, *Yersinia enterocolitica* CMC 120 and *Escherichia coli* DM] and three yeasts [*Kluvyeromyces fragilis* A 230, *Saccharomyces cerevisiae* WET 136 and *Candida albicans* ATCC 1023]. These microorganisms were provided from the Microbiology Laboratory Culture Collection, Department of Biology, Kahramanmaraş, Sütcü Imam University, Turkey. Antimicrobial activities of the ligands and their mixed-ligand Cu^{II} complexes were determined using the agar-disc diffusion method as will be described below. The bacteria were first incubated at 37 ± 0.1 °C for 24 h in nutrient broth (Difco), and the yeasts were incubated in *sabouraud dextrose* broth (Difco) at 25 ± 0.1 °C for 24 h. The cultures of the bacteria and yeast were injected into the petri dishes (9 cm) in 0.1 cm^3. Then, mueller hinton agar and sabouraud dextrose agar (sterilized in a flask and cooled to 45–50 °C) were homogenously distributed onto the sterilized petri dishes to the extent of 15 cm^3. Subsequently, the sterilized blank paper discs of 6 mm diameter were saturated with 1200 μg of chemical matters per disc. The discs were placed on to the agar plates, which had previously been inoculated with the above organisms. In addition, blank paper discs

treated with ampicillin, streptomycin and nystatin antibiotics were used as positive controls. Afterwards the plates combined with the discs were left at 4 °C for 2 h, the plates injected with yeast were incubated at 25 ± 0.1 °C for 24 h, and ones injected with bacteria were incubated at 37 ± 0.1 °C for 24 h. After 24 h, inhibition zones appearing around the discs were measured and recorded in mm. The initial number of microorganisms in the suspension was determined for the total yeasts and bacterial count during 24 h at 37 °C for bacteria and 48 h 25 °C for yeasts [17].

Potentiometric studies

Reagent and solutions

Stock solutions of Schiff bases derived from 2,6-diformyl-4-*t*-butylphenol and 2.6-di-formyl-4-methylphenol with aromatic amines were prepared in dioxan (Merck, extra pure). The purity was checked by the Gran method with standard HCl [18]. Carbonate-free KOH solutions (Merck, extra pure) were prepared with freshly boiled doubly-deionised water under a nitrogen atmosphere in 60% dioxan-water mixtures. The alkali titre and absence of carbonate were periodically checked by pH-meter, using the appropriate Gran function [18] against primary standard oven-dried potassium hydrogen phthalate. Acid solutions prepared from Merck p.a. HCl acid were titrated against standardised KOH. The KCl used as a background electrolyte was a Merck p.a. reagent. The ionic strength of each solution was adjusted to 0.1 mol.dm^{-3} by the addition of KCl as supporting electrolyte.

Potentiometric measurement

The measurements in this study were carried out at 25.00 ± 0.02 °C in water-dioxan mixtures containing 60% dioxan (v/v). For potentiometric titrations we used a special glass vessel with a double wall, with entries for the combined glass electrode (Mettler Toledo In lab 412), nitrogen and base from burette (Orion 960 automatic titrator). The emf measurements were made with Orion EA 940 pH meter (resolution 0.1 mV, accuracy 0.2 μl). The waiting period was 3 min. The electrode was modified by replacing its aqueous KCl solution with 0.1 M KCl saturated with AgCl. Temperature was maintained constant inside the cell at 25.00 ± 0.02 °C, by a water circulation proceeding water from a thermostatted bath. The system was calibrated daily to read hydrogen ion concentration by the titration of a strong acid (HCl, 0.1 M) with a strong base (KOH, 0.1 M) at the same ionic strength to assure that we got adequate responses in the studied pH range. The protonation constants of Schiff bases were determined by pH-potentiometric titration and the total volume was 50.00 ± 0.01 cm^{-3} at the beginning of each potentiometric titration. The mixtures containing 0.1 M KCl and 4.0×10^{-3} M HCl plus 1.5×10^{-3} M Schiff bases were titrated by incremental additions of carbonate-free and standard KOH. Titrations were performed over the pH range 2.0–12.0. There were no precipitation in the pH range in which titrations were performed.

Treatment of potentiometric data

Equilibrium constants were evaluated by iterative non-linear least squares fit of potentiometric equilibrium curves through mass balance equations for all the components expressed in term of known and unknown equilibrium constants using a computer program BEST [19]. All the models converged at $\sigma < 0.02$ pH units the observed pH values, which is considered to be an acceptable fit. The equilibrium constants reported in this paper were obtained as averaged values of three titrations.

Results and discussion

Symmetric dinucleating ligands can only lead to minor differences in the metal environment upon complexation, and this is always due to the steric constraints imposed by other ligands or by the metals themselves. Therefore, a necessary step towards the synthesis of appropriate models for dinuclear metallo-proteins and -enzymes is the preparation of dinucleating ligands that can provide chemically distinct donor sets. The analytical data for the ligands and their mixed-ligand Cu^{II} complexes are listed in Table 1 and agree very well with the molecular formula proposed. The Schiff base derivatives were prepared by the condensation of 4-methyl-2,6-diformylphenol and 4-*t*-butyl-2,6-diformylphenol with aniline derivatives (1:2 molar ratio, carbonyl:amine) in absolute EtOH. The purity of these compounds was confirmed by a t.l.c. method. The complexes having the general formula $[Cu_2(L^n)Cl_3]$ were prepared in high yield from the reaction of copper(II) chloride di-hydrate with the Schiff base ligands (HL^1 – HL^6). Moreover, the complexes with type $[Cu_2(L^n)(dp)_2]3Cl$ were also obtained in normal yield from the reaction of the complexes $[Cu_2(L^n)Cl_3]$ with the 2,2′-dipyridyl (dp) ligand in the EtOH solution. The Schiff base ligands HL^5 and HL^6 have been obtained from the amine derivative containing the OH group. The complexes with dp have a cationic nature and therefore their properties are different from other complexes. For instance, their solubility is higher than other Cu^{II} complexes. Symmetric dinucleating ligands can only lead to minor differences in the metal environment upon complexation, and this is always due to steric constraints imposed by other ligands or by the metals themselves. Therefore, a necessary step towards the synthesis of appropriate models for dinuclear metallo-proteins and -enzymes is the preparation of dinucleating ligands that can provide chemically distinct

Table 1. Analytical and physical data for the Schiff Base ligands and their Cu^{II} complexes.

Compound	Colour	Yield (%)	M.p. (°C)	Found (calcd.)% C	N	H	Cl	Cu
HL^1	light brown	68	140	53.4 (53.5)	5.3 (5.1)	3.4 (3.3)	–	–
$[Cu_2(L^1)(dp)_2]3Cl$	green	58	>250	52.7 (52.8)	7.9 (8.0)	3.9 (3.8)	15.0 (15.1)	18.1 (18.0)
$[Cu_2(L^1)Cl_3]$	light brown	69	>250	35.7 (35.6)	3.9 (4.0)	2.1 (2.0)	15.1 (14.9)	18.0 (18.4)
HL^2	orange	67	171	56.0 (55.9)	5.4 (5.3)	4.3 (4.5)	–	–
$[Cu_2(L^2)(dp)_2]3Cl$	black	56	>250	52.7 (54.6)	7.6 (7.5)	4.5 (4.4)	14.2 (14.3)	17.1 (17.0)
$[Cu_2(L^2)Cl_3]$	light brown	68	>250	38.6 (38.5)	3.7 (3.8)	2.8 (2.9)	14.3 (14.7)	17.0 (17.3)
HL^3	light brown	69	105	80.7 (80.5)	8.2 (8.1)	6.4 (6.2)	–	–
$[Cu_2(L^3)(dp)_2]3Cl$	black	60	>250	51.5 (51.6)	8.2 (8.3)	3.0 (3.1)	15.9 (15.8)	18.9 (18.8)
$[Cu_2(L^3)Cl_3]$	brown	65	215	48.0 (47.9)	4.9 (5.0)	3.6 (3.3)	18.5 (18.1)	22.1 (22.3)
HL^4	orange	69	115	81.2 (81.3)	7.2 (7.3)	7.2 (7.0)	–	–
$[Cu_2(L^4)(dp)_2]3Cl$	green	59	248	53.5 (53.4)	7.9 (7.8)	4.1 (4.2)	14.9 (14.8)	17.6 (17.7)
$[Cu_2(L^4)Cl_3]$	light brown	67	>250	50.6 (50.5)	4.5 (4.4)	4.4 (4.6)	17.3 (17.0)	20.6 (20.8)
HL^5	dark brown	68	180	72.8 (72.9)	8.1 (8.0)	5.2 (5.3)	–	–
$[Cu_2(L^5)(dp)_2]3Cl$	brown	62	253	50.1 (50.0)	7.8 (7.7)	3.1 (3.2)	14.7 (14.8)	17.7 (17.6)
$[Cu_2(L^5)Cl_3]$	black	69	>250	43.5 (43.5)	4.8 (4.7)	2.9 (3.0)	18.4 (18.7)	21.9 (22.0)
HL^6	brown	65	162	74.2 (74.1)	7.2 (7.2)	6.2 (6.2)	–	–
$[Cu_2(L^6)(dp)_2]3Cl$	green	58	235	52.4 (52.5)	7.2 (7.2)	4.2 (4.1)	13.8 (13.7)	16.4 (16.3)
$[Cu_2(L^6)Cl_3]$	black	66	>250	46.4 (46.5)	4.5 (4.6)	3.7 (3.8)	17.1 (17.3)	20.4 (20.5)

donor sets. Synthesized Schiff bases and complexes are stable at room temperature unless decomposition occurs. The general formula of the ligands and their Cu^{II} complexes used for the R_1 and R_2 substituents are given in Figure 1.

The Schiff bases and their Cu^{II} complexes are soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, MeOH, EtOH, THF and DMSO. The reaction of the ligand derivatives HL^1-HL^6 with metal halide leads to the formation of the $[Cu_2(L^n)Cl_3]$ and [Cu2(Ln)(dp)2]3Cl derivatives. The elemental analyses were satisfactory and show that the complexes have a ligand-to-metal ratio of 1:2 and 1:2:1. The complexes have two different bridged positions: (i) in the $[Cu_2(L^n)Cl_3]$ complex, one of them is the phenolic group (μ-oxo) of the Schiff base ligands, and the other is the chloro-bridge (μ-chloro), (ii) in the $[Cu_2(L^n)(dp)_2]3Cl$ complex, when the dp ligand is added to the solution of the $[Cu_2(L^n)Cl_3]$ complexes, the chloro bridge can be replaced by the dp which is not a bridge ligand.

The most important i.r. spectral bands of the free Schiff bases are given in Table 2. The Schiff bases show intramolecular hydrogen bonding (O—H···N) by virtue of broad absorption bands within the 3449–3188 cm^{-1} range [21]. The bands due to the OH modes are no longer observed, in the spectra of the complexes, denoting that the hydroxyl proton is displaced by Cu^{II} ions, leading to covalent Cu—O bonding with the ligands. In the complexes of the ligands HL^5 and HL^6, the hydroxyl groups of the amine moiety are not coordinated to the Cu^{II} ions, therefore these groups are still observed in the 3400–3350 cm^{-1} range. The bands of the ν(t-Bu) and $\delta(CH_3)$ groups

Table 2. I.r. spectral data[a] for the ligands and their metal complexes (cm^{-1})

Compound	ν(OH)	ν(CH=N)	ν(C—OH)	ν(M—N)	ν(M—O)
HL^1	3447	1622	1315	–	–
$[Cu_2(L^1)Cl_3]HL$	–	1625	1334	424	501
$[Cu_2(L^1)(dp)_2]HL3Cl$	–	1598	1305	465	494
HL^2	3445	1622	1359	–	–
$[Cu_2(L^2)Cl_3]HL$	–	1608	1320	459	520
$[Cu_2(L^2)(dp)_2]HL3Cl$	–	1601	1355	443	526
HL^3	3445	1622	1315	–	–
$[Cu_2(L^3)Cl_3]HL$	–	1629	1328	434	557
$[Cu_2(L^3)(dp)_2]HL3Cl$	–	1595	1321	424	542
HL^4	3443	1622	1360	–	–
$[Cu_2(L^4)Cl_3]HL$	–	1631	1363	415	511
$[Cu_2(L^4)(dp)_2]HL3Cl$	–	1631	1361	417	490
HL^5	3188	1618	1366	–	–
$[Cu_2(L^5)Cl_3]HL$	–	1631	1334	435	520
$[Cu_2(L^5)(dp)_2]HL3Cl$	–	1631	1365	430	510
HL^6	3240	1620	1346	–	–
$[Cu_2(L^6)Cl_3]HL$	–	1635	1400	451	532
$[Cu_2(L^6)(dp)_2]HL3Cl$	–	1631	1380	460	497

[a] cm^{-1}.

Table 3. The electronic absorption spectral, magnetic moments and molar conductance data of the ligands and their complexes

Compound	μ_{eff} (B.M.) per Cu(II)	λ_{max} (nm)	Λ^a
HL^1	–	374, 350, 318, 292	1.2
$[Cu_2(L^1)Cl_3]HL$	1.05	796, 369, 345, 304, 238	12.7
$[Cu_2(L^1)(dp)_2]HL3Cl$	1.83	657, 411, 369, 312, 295,234	67.4
HL^2	–	451, 367, 364, 348, 329, 316, 285	1.3
$[Cu_2(L^2)Cl_3]HL$	1.03	741, 477, 437, 411, 357, 338, 319, 241	10.8
$[Cu_2(L^2)(dp)_2]HL3Cl$	1.77	643, 437, 401, 356, 335,298, 246	65.1
HL^3	–	489, 342, 335, 313, 290, 226	1.1
$[Cu_2(L^3)Cl_3]HL$	1.10	739, 617, 465, 380, 318, 267	26.7
$[Cu_2(L^3)(dp)_2]HL3Cl$	1.74	644, 421, 310, 296, 245,217	71.8
HL^4	–	372, 340, 314, 286, 218	1.4
$[Cu_2(L^4)Cl_3]HL$	1.06	585, 480, 395, 294, 288, 230	13.2
$[Cu_2(L^4)(dp)_2]HL3Cl$	1.80	620, 422, 311, 285, 240	68.5
HL^5	–	380, 330, 296, 230	1.4
$[Cu_2(L^5)Cl_3]HL$	1.15	839, 526, 412, 397, 358, 305,278, 269, 230	31.5
$[Cu_2(L^5)(dp)_2]HL3Cl$	1.76	662, 465, 421, 310, 294,244	69.7
HL^6	–	378, 331, 297, 225	1.7
$[Cu_2(L^6)Cl_3]HL$	1.20	696, 501, 406, 347, 308, 279	15.9
$[Cu_2(L^6)(dp)_2]HL3Cl$	1.78	617, 442, 354, 312, 297, 236	66.3

[a] Ω^{-1} cm^2 mol^{-1}.

are observed in the 2960–2950 and 2925–2915 cm^{-1} range respectively. In the spectra of the ligands HL^1–HL^6, the observed strong bands in the 1635–1595 cm^{-1} range may be assigned to the ν(CH=N) stretching. In the $[Cu_2(L^n)Cl_3]$ complexes, these vibration are shifted to the lower regions and this situation confirms that the nitrogen atom of the azomethine group is coordinated to the Cu^{II} ions. In the i.r. spectra of the $[Cu_2(L^n)(dp)_2]3Cl$ complexes a second azomethine stretching due to the dp in the 1630–1620 cm^{-1} range is observed. The strong ligand bands around 1625–1615 cm^{-1} can be attributable to the azomethine ν(C=N) stretching. The i.r. spectra of the Schiff bases exhibit bands in the 1350–1255 cm^{-1} region assignable to the phenolic ν(C—O) vibration [22, 23]. In the complexes, this vibration shifts to lower regions and their peak intensity due to the ν(C—OH) vibration decreases. The evidence indicates that the oxygen atom of the phenolic (C—OH) group is coordinated to the Cu^{II} ions. The bonding of Cu^{II} ions to the ligands through the nitrogen and oxygen atoms is further supported by the presence of new bands in the 557–417 cm^{-1} range due to ν(M—O) and ν(M—N) vibrations.

Equivalent conductance of chloride complexes $[Cu_2(L^n)Cl_3]$ carried out in 1×10^{-3} M methanol solutions are in the range 10.8–31.5 Ω^{-1} cm^2 mol^{-1} suggesting that the chloride ions are inside the coordination sphere. From these data, we suggest the non-electrolyte nature of the complexes. Moreover, the equivalent conductances of the mixed-ligand binuclear complexes $[Cu_2(L^n)(dp)_2]3Cl$ were carried out in methanol and the values were found to be in the 65.1–71.8 Ω^{-1} cm^2 mol^{-1} range, and from these data we can say that these complexes have the cationic nature and conduct electricity in solution [20]. This indicates that the chloride ions are not coordinated to the metal in solution. The complexes of the ligands HL^3, HL^5 and HL^6 have the highest conductivity (see Table 3).

The electronic spectral data of the ligands and complexes are given in Table 3. The u.v.–vis spectra of the metal complexes of the HL^5 and HL^6 ligands in EtOH solution showed a high intensity broad band in the 480–401 nm range which is tentatively assigned to ligand (π)- metal (d) charge-transfer, while the weaker ligand field bands may be obscured by such transitions. The copper(II) complexes of these compounds are assigned to basically square-planar ligand environments in essentially discrete $[Cu_2(L^n)Cl_3]$, although the observed energies are somewhat lower than those generally quoted for square-planar copper(II) complexes. A comparison of the electronic spectra of the free ligands with those of the corresponding metal complexes showing some shift were detected, and this can be considered as evidence for the complex formation. The complexes $[Cu_2(L^n)Cl_3]$ and $[Cu_2(L^n)(dp)_2]3Cl$ show intense bands around the ~350–340 nm range attributable to the π–π^* transition associated with the azomethine linkage [24]. The u.v. spectral features of the azomethine group with the *o*-phenylene bridge and the spectra show the three absorption bands in the 410–364 nm range.

The magnetic behaviour of the $[Cu_2(L^n)Cl_3]$, series varies from very weak paramagnetism to only slightly depressed paramagnetism. The magnetic moments (Table 4) of the copper(II) complexes all fall in the normal range for a copper(II) species with $S = 1/2$. Magnetic moment values vary from 1.03–1.20 B.M and this confirms that the copper(II) complexes have square-planar geometry. In other words, the mixed ligand Cu^{II} complexes $[Cu_2(L^n)(dp)_2]3Cl$ have the magnetic moment data in the 1.74–1.83 B.M. range at room temperature. This indicates that the copper(II) ions in the complexes and of a tetrahedral nature [25].

The ^{1}H and ^{13}C-n.m.r. spectra have been recorded and used $CDCl_3$ as solvent. Peak assignments were made by peak integration and multiplicity. The

Table 4. The ^{1}H (^{13}C)-NMR Data (as ppm) For The Schiff base ligands

Chemical Shift (δppm) Compound	CH_3	Quarternary C atom	$C(CH_3)$	Ar	CH=N	OH
HL^1	2.39 (20.70)	–	–	6.90–7.18 (121.80–157.71)	8.14 (164.97)	14.45
HL^2	–	1.32 (30.86)	34.30	6.20–7.20 (120.45–157.22)	8.20 (163.70)	15.05
HL^3	2.42 (21.07)	–	–	6.35–7.44 (120.15–157.47)	8.33 (162.80)	13.70
HL^4	–	1.38 (31.25)	34.45	6.27–7.43 (120.88–156.95)	8.37 (164.64)	14.40
HL^5	2.36	–	–	6.20–7.19 (116.72–157.51)	8.34 (164.64)	12.15
HL^6	–	1.35 (30.16)	34.90	6.85–7.18 (119.24–156.77)	8.30 (165.97)	12.75

^{1}H- and ^{13}C- n.m.r. data of the ligands are given in Table 4. In the ^{1}H- n.m.r. spectra of the ligands, the singlets in the 15.05–12.15 ppm range can be attributed to the proton of the –OH group. This peak disappears together with addition of the D_2O. In the ligands HL^5 and HL^6, the –OH group of the aniline moiety is shown at 11.53 and 10.23 ppm as a singlet, respectively. The proton of the azomething group is shown in the 8.14–8.33 ppm range as a singlet. The multiplets in the 6.20–7.44 ppm range can be assignable to the protons of the aromatic rings. The singlets in the 2.30–2.40 ppm range and in the 1.32–1.38 ppm range may be assigned to the protons of the $–CH_3$ and $–C(CH_3)_3$ groups [26].

In the spectra of the ^{13}C-n.m.r., the resonances in the 162.15–165.97 ppm range may be assigned to the carbon atoms of the CH=N group. The aromatic carbon atoms are shown in the 116.72–157.71 ppm range. The carbon atoms of the $—CH_3$ and $—C(CH_3)_3$ groups have been determined in 20.70–20.72 and 30.86–31.15 ppm ranges. In the ligands HL^2, HL^4 and HL^6, the quarternary carbon atoms are determined in the 34.90–34.45 ppm range.

The positive–ion FAB mass spectra of the Schiff bases show peaks in m/z 343–515 (% 40–50) range and these peaks may be due to the molecular ion peaks ([M]+). In the spectra of the ligands HL^1, HL^3 and HL^5, the peaks in the m/z 298 (% 100), 457 (% 100) and 332 (% 100) can be attributed to the loss of the CH_3 groups. In the spectra of the ligands HL^2, HL^4 and HL^6, the highest intensity peaks in the m/z 328 (% 100), 458 (% 100) and 332 (% 100) may be assigned to the loss of the $C(CH_3)_3$ group.

We have examined the catalytic activity of the mixed-ligand Cu^{II} complexes for oxidation of the catechol and ascorbic acid by O_2 to *o*-benzoquinone and 5-[(R)-1,2-dihydroxyethyl]furan-2,3,4-(5H)-trione, respectively, in air-saturated dichloromethane (DCM) according to the reaction (Figure 2):

The reactivity studies were performed in a DCM-MeOH solvent mixture because of the good solubility of the complexes as well as of the substrate and of its product. No base was added to the solutions to avoid the auto-oxidation of the substrate by air in the presence of base. The above catalytic oxidation does not proceed in the absence of the catalysts, the mixed-ligand Cu^{II} complexes. The catechol and copper(II) complex have to form a Cu^{II} catecholate intermediate before electron transfer from catechol to the Cu^{II} atoms can occur. If the coordinating molecule is a stronger ligand than the catechol, no oxidation will be observed. In our studies, the fifth coordination site is occupied by an solvent molecule (MeOH, Figure 3). All these are capable of being replaced by catechol. The fifth ligand must be released before the association of oxygen and the oxidation of the catechol is possible. According to this the reaction rate depends on the lability of the fifth ligand [27]. It is necessary to get an estimation of the ability of the complexes to oxidize catechol. For this purpose, 10^{-4} mol dm^{-3} solutions of the mixed-ligand complexes $[Cu_2(L^n)(dp)_2]3Cl$ (n: 1, 2, 3, 4, 5 and 6) were treated with 50 equivalents of

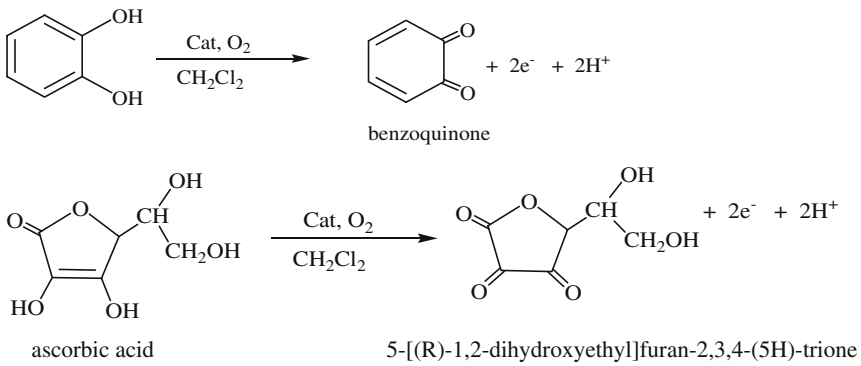


Fig. 2. Oxidation of catechol and ascorbic acid by air using a catalyzer.

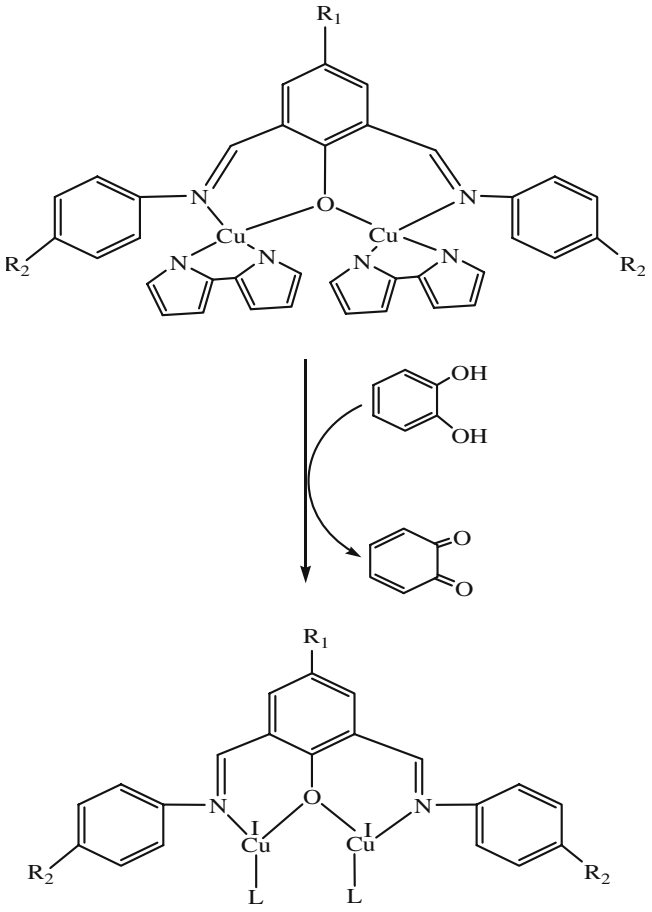


Fig. 3. Proposed course of reaction of the mixed-ligand Cu^{II} complexes in MeOH.

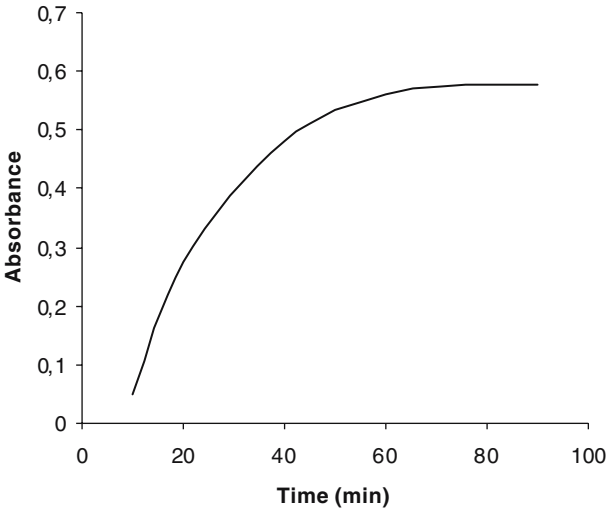


Fig. 4. Time-dependent formation of substituted quinones in presence of the complex $[Cu_2(L^6)(dp)_2]3Cl$ at 25 °C.

catechol under aerobic conditions. The course of the reaction is followed by UV-vis spectroscopy. The UV-vis spectra of the original solution directly after the addition and after 2, 4, 6, 8, 10, 12 h and up to 48 h were recorded and corrected for volume changes. The increase in the absorption at 390 nm, all the complexes $[Cu_2(L^n)(dp)_2]3Cl$ showed considerable catecholase activity. The oxidation of catechol by the complexes increases in the *o*-benzoquinone absorption band at 390 nm. This adduct reacts with dioxygen to form the starting dicopper(II) complex and the oxidised substrate. The catalytic activity largely depends on the structure of the complex, and the general trend is the same for ascorbic acid and catecol. The planar dinuclear complexes with a large Cu–Cu distance (greater than 5 °A) show practically no catalytic activity, whereas non-planar dinuclear complexes with an equivalent coordination site at an appropriate distance (3–4 °A) catalyse the reaction. In our mixed-ligand dinuclear Cu^{II} complexes, the activity order is: $[Cu_2(L^6)(dp)_2]3Cl > [Cu_2(L^5)(dp)_2]3Cl > [Cu_2(L^2)(dp)_2]3Cl > [Cu_2(L^1)(dp)_2]3Cl > [Cu_2(L^4)(dp)_2]3Cl > [Cu_2(L^3)(dp)_2]3Cl$. This situation is shown in Figure 4.

From the data obtained in Figure 4, among all the complexes, while the complex $[Cu_2(L^6)(dp)_2]3Cl$ shows the highest activity and the complex $[Cu_2(L^3)(dp)_2]3Cl$ shows the lowest activity, from which one can infer that the catecholase activity is decreasing with increasing bulky substituents and functional groups with coordinating ability in the side chain of the Schiff base ligand. The bands in the charge-transfer region as well as the d-d bands remain unchanged with respect to position and intensity. Therefore, binding of catechol to the dinuclear copper(II) centre can be definitely excluded. In our study, after addition of the catechol, in the charge-transfer region of *ca*. 350–450 nm the intensity decreases, simultaneously a new weak band appears at *ca*. 500 nm.

The maximum of the d–d bands shifts from 662–617 nm range to higher wavelength. The catecholase activity of binuclear copper(II) complexes has been studied with the help of electronic spectroscopy by monitoring the appearance of the absorption maximum of the substituted quinone product ($\lambda_{max} = 390$ nm).

The kinetic studies of the oxidation of catechol were carried out by the method of initial rates by monitoring the increase in the characteristic quinone (*o*-benzoquinone) absorption band at 390 nm as a function of time. Under anaerobic conditions, little product was formed, so the solvent was saturated with O_2 before conducting the kinetic experiments. Oxygen participates directly in the catalytic cycle reoxidizing any generated copper(I) species back to the active copper(II) complex. A catalytic activity is observed since after 10 min an increase in absorption at 390 nm of *ca*. 0.23 units was observed, which corresponds to a turnover of more than 5 equivalents of *o*-benzoquinone. Under these experimental conditions, saturation kinetics were found for the absorbance *versus* the reaction time (Figure 4).

Reaction of ascorbic acid with the mixed-ligand binuclear Cu^{II} complexes was examined under nitrogen. The reduction process was monitored by measuring the changes in absorbance of the d–d bands of the

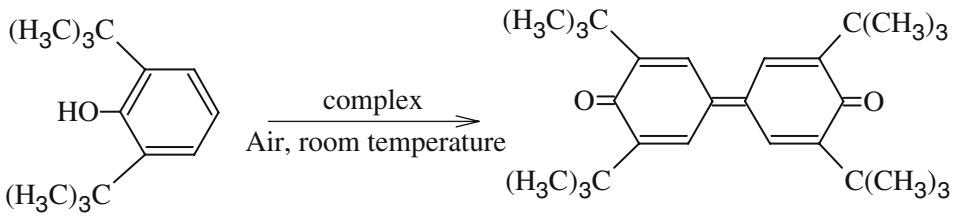


Fig. 5. Oxidative Carbons Coupling of the Sterically bindered phenol 2,6-di-t-butylphenol.

complexes. Figure 6 shows the spectral change due to the addition of ascorbic acid. The d–d bands of the complexes $[Cu_2(L^n)(dp)_2]3Cl$ in the 662–617 nm range disappear on addition of ascorbic acid under nitrogen, reappearing when the solution is exposed to air. It has been shown that only Cu^{II} complexes with distorted tetrahedral structure are reduced to Cu^{I} by ascorbic acid. Planar Cu^{II} complexes are not reduced by these two-electron donors. Reduction of Cu^{II} complexes by ascorbic acid is therefore indirect evidence for the distorted tetrahedral structure of the complexes. This has been inferred from spectral data. Moreover, because of other complexes $[Cu_2(L^n)Cl_3]$ in this study have a square-planar geometry, we did not investigate their reaction with ascorbic acid.

We have examined the catalytic activity of the binuclear complexes $[Cu_2(L^n)Cl_3]$ and $[Cu_2(L^n)(dp)_2]3Cl$ for oxidation of 2,6-di-*t*-butylphenol by air O_2 to 2,2′-di-*t*-butyl-4,4′-diphenolquinone (DTBD) in air saturated DCM according to the reaction in Figure 5.

All complexes in the catalysis reaction are soluble in the DCM-methanol solvent mixture. If they are not also soluble in this mixture, there is no problem, because, this type reactions can occur at the heterogen or homogen phase in the similar way. As the oxidative carbon-carbon coupling of the sterically hindered phenol 2,6-di-*t*-butylphenol lead to diphenoquinones is in radical mediated reactions, we have studied the mixed-ligand binuclear Cu containing radicals for oxidative studies with 2,6-di-*t*-butylphenol. When the phenols (2 mmol) are added to the complexes (0.01 mmol) in DCM-MeOH (1:1) solvent mixture (50 cm^3), the dark brown or black turns to red or light red in the presence of air. It was found that after 55–78 h, 100% phenols were converted to the 3,3′4-5,5′-tetra-*t*-butyl-4,4′-diphenolquinone for the mixed-ligand Cu^{II} complexes. For the compound 2,6-di-*t*-butylphenol, the best oxidant is the complexes of the ligands HL^5 and HL^6. Moreover, the complexes of the ligands HL^3 and HL^4 are the worst oxidant for the sterically hindered phenol. These two different situations can be explained by the properties of the ligands. In the *p*- position of the amine fragments of the ligands ligands HL^5 and HL^6, the —OH groups have electron-donor properties with a mesomeric effect and therefore the activity of the complexes increases. In other words, in the ligands HL^3 and HL^4, there are Br atoms in the position of the —OH group. The atom Br attracts the electron with induction (its mesomeric property is poor) and the reactivity of the complexes decreases. The complexes of the ligands ligands HL^1 and HL^2 show similar properties with the complexes of the ligands HL^5 and HL^6. Order of the oxidizing of the complexes is: $[Cu_2(L^6)(dp)_2]3Cl \geq [Cu_2(L^5)(dp)_2]3Cl > [Cu_2(L^2)(dp)_2]\ 3Cl \geq [Cu_2(L^1)(dp)_2]3Cl > [Cu_2(L^4)(dp)_2]3Cl \geq [Cu_2(L^3)(dp)_2]3Cl$. The spectral properties of the $[Cu_2(L^6)(dp)_2]3Cl$ are shown in Figure 6. The course of the reaction was followed by optical spectroscopy, as TTBD shows a characteristic peak in the electronic spectrum at 425 nm, as seen also from Figure 6. Such changes in the electronic spectra of the complexes at different time intervals were monitored by removing the catalyst from the reaction solution. At the end of the oxidative coupling, the properties of the complexes changed.

The potentiometric titration curves of the 2,6-di(4-bromo-phenyliminomethyl)-4-methylphenol (HL^3) and 2,6-di(4-hydroxyphenyliminomethyl)-4-methylphenol (HL^5) are given in Figure 7. The examination of potentiometric titration curve of 4-methyl-2,6-di(4-methyliminomethyl) phenol shows two inflections at $x = 2$ and $x = 3$, due to dissociable of protons corresponding in separate steps. A break near $x = 2$ can be explained by the simultaneous dissociation of two protons from protonated form of the Schiff bases in these pH ranges. The second inflection at near $x = 3$ proved that HL^1 has three dissociable protons. Figure 7 indicates the potentiometric titration curve as a function of added KOH (x = moles of base added per mole of ligand present) at 25.00 ± 0.02 °C and $\mu = 0.1$ M KCl. The stoichiometric protonation constants of Schiff bases derived

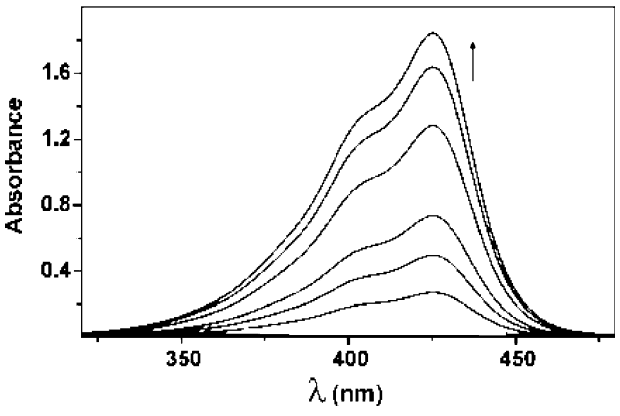


Fig. 6. The electronic spectra of the complexes $[Cu_2(L^6)(dp)_2]3Cl$ for the C—C coupling reaction of the 2,6-di-*t*-butylphenol.

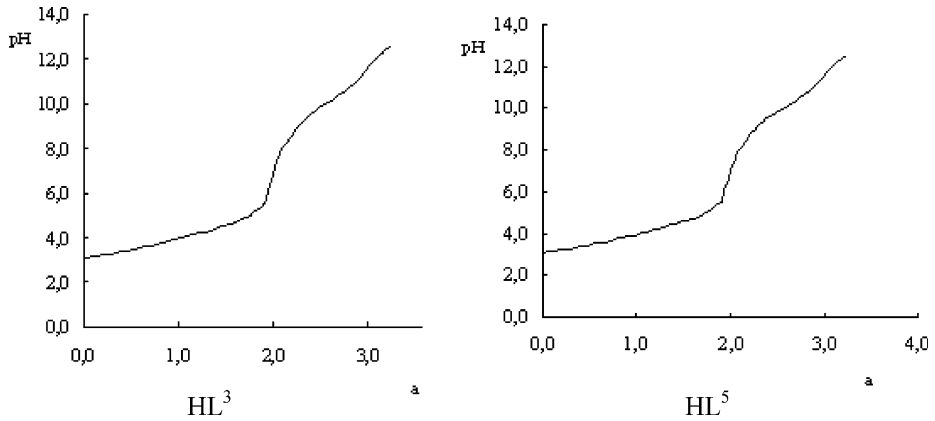


Fig. 7 Potentiometric titration curve for 2,6-di(4-bromophenyliminomethyl)-4-methylphenol (HL^3) and 2,6-di(4-hydroxyphenyliminomethyl)-4-methylphenol (HL^5) at 25 ± 0.1 °C μ = 0.1 M KCl (a = moles of KOH added per mole of the ligand).

Table 5. The stoichiometric protonation constants of Schiff Bases at 25.00 ± 0.02 °C for 60% dioxan-H_2O Mixture (μ = 0.1 M KCl)

Symbol	$LogK_{OH}$	$LogK_{NH(1)}$	$LogK_{NH(2)}$
HL^1	9.84 ± 0.05	4.42 ± 0.04	3.09 ± 0.01
HL^2	8.30 ± 0.05	2.82 ± 0.04	1.75 ± 0.01
HL^3	8.46 ± 0.05	2.88 ± 0.04	1.95 ± 0.01
HL^4	8.26 ± 0.05	2.19 ± 0.04	1.89 ± 0.01
HL^5	9.75 ± 0.05	4.43 ± 0.04	3.22 ± 0.01
HL^6	8.94 ± 0.05	3.44 ± 0.04	2.78 ± 0.01

from dicarbonyl compounds with aromatic amines in %50 dioxan-water mixtures at 25.00 ± 0.02 °C and their standard deviations have been given in Table 5. The ligands, in their fully protonated form $[H_3L]^{2+}$, have three dissociable protons. The logKOH values correspond to the protonation equilibrium of phenolic oxygen ions and $LogK_{NH(1)}$ and $LogK_{NH(2)}$ values to imine nitrogen atoms. In general, the factors that influence the basicity of compounds are: (1) inductive effects (2) steric effects (3) hydrogen bonding and (5) resonance effects. In this work, we observed that with regard to the basicity of Schiff bases in dioxan, inductive, hydrogen bonding and resonance effects are strong. These are discussed below in detail. The values tabulated in Table 5 show that the protonation constants of bromine substituted Schiff bases are lower than those of methyl substituted ones.

This can be explained by the electron withdrawing effect of bromine from the benzene ring through the inductive effect and electron-donating effect of methyl through resonance and inductive effects. The difference between the protonation constants of Schiff bases 2,6-diformyl-4-*t*-butylphenol (HL^2, HL^4 and HL^6) and 2,6-di-formyl-4-methylphenol (HL^1, HL^3 and HL^5) can be explained by the steric effect. The fact that the protonation constants of imine nitrogens present were different at a dimension of one logarithmic unit unlike the expectations of closely spaced values is due to hydrogen bonding. The protonation constant (log $K_{NH(2)}$) decreased due to the fact that one of the two imine nitrogens in the Schiff base is protonated ($logK_{NH(1)}$) while the other makes a strong hydrogen bond with the hydrogen of the phenolic oxygen.

Antibacterial activities of the ligands and the complexes have been carried out against the thirteen bacteria [*Corynebacterium xerosis* UC 9165, *Bacillus brevis* NRS, *Bacillus megaterium* DSM 32, *Bacillus cereus* EU, *Mycobacterium smegmatis* CCM 2067, *Staphylococcus aureus* Cowan 1, *Pseudomonas aeruginosa* ATCC 27853, *Klebsiella pneumoniae* FMC 5, *Enterococcus faecalis* ATTC 15753, *Micrococcus luteus* LA 2971, *Yersinia enterocolitica* CMC 120 and *Escherichia coli* DM] and three yeasts [*Kluvyeromyces fragilis* A 230, *Saccharomyces cerevisiae* WET 136 and *Candida albicans* ATCC 1023] [17]. The test solutions were prepared in $CHCl_3$. The results of the antibacterial activities are summarised in Table 6. The synthesized compounds were found to have remarkable bacterial and fungicidal properties; it is however interesting that the biological activity gets enhanced on undergoing complexation with the metal ion. From the structure point of view of the prepared compounds with their effects on microbial tested, it is clear that formation of the chelate derivatives in the 1:2 molar ratio (L:M) sometimes increase the biological activity as appeared from the mixed-ligand Cu^{II} complexes. Moreover, the enhanced activities of the metal complex derivatives compared to the free ligands may be due to the chloride ion around the central metal ion arising from chelation in 1:2 molar ratio (L:M). Such an increased activity for the metal chelates as compared to the free ligands can be explained on the basis of chelation theory [29]. Chelation considerably reduces the polarity of the metal ion because of the partial sharing of its positive charge with the donor groups and possible *p*-electron delocalisation over the chelate ring. Such chelation could increase the lipophilic character of the central metal atom, which subsequently favours the permeation through the lipid layer of cell membrane. The mode of action of the complexes may involve the formation of the hydrogen bond through the azomethine

Table 6. Antimicrobial activity data for the Schiff base ligands and their metal complexes.

Compound	Gram positive bacteria								Gram negative bacteria									
	1	2	3	4	5	6	7	8	1′	2′	3′	4′	5′	6′	7′	A10[b]	S10[c]	N100[d]
X[a]																		
HL^1	f		f	f	5	7	f	f	f	8	f	9	8	f	f	9	7	5
$[Cu_2(L^1)Cl_3]$	f	14	f	13	f	23	f	f	f	21	24	15	20	f	30	16	19	NT
$[Cu_2(L^1)(dp)_2]3Cl$	f	17	17	15	9	19	16	f	10	18	24	20	24	20	30	14	16	NT
HL^2	f	f	f		f	6	f	f	f	f	30	f		f	30	13	15	NT
$[Cu_2(L^2)Cl_3]$	f	10	f	19	10	15	f	f	f	f	18	12	13	f	30	20	21	NT
$[Cu_2(L^2)(dp)_2]3Cl$	16	13	10	22	17	18	f	19	12	14	19	19	20	f	20	12	14	NT
HL^3	f	f	f	5	3	7	f	f	f		18		f	f	18	25	22	NT
$[Cu_2(L^3)Cl_3]$	f	5	8	11	14	15	7	f	6	9	7	10	10	f	6	33	23	NT
$[Cu_2(L^3)(dp)_2]3Cl$	f	10	14	14	17	22	17	13	11	11		18	14	17	12	17	15	NT
HL^4	f	f	f	6	5	6	f	f	f	5	26		5	f	27	8	10	9
$[Cu_2(L^4)Cl_3]$	7	12	f	13	14	12	f	f	f	11	28	9	16	f	30	10	13	NT
$[Cu_2(L^4)(dp)_2]3Cl$	16	20	14	17	18	20	10	14	f	15	21	14	19	11	14	17	16	NT
HL^5	f	f	f	6	5	8	f	f	f	6	20	6	9	f	20	15	20	NT
$[Cu_2(L^5)Cl_3]$	13	13	11	12	12	15	20	18	17	14	17	17	21	27	25	30	22	NT
$[Cu_2(L^5)(dp)_2]3Cl$	15	20	16	15	15	21	18	15	17	19		21	27	25		10	7	–
HL^6	f	f	f	4	4	6	f	f	f	5		7	7	f		NT	NT	15
$[Cu_2(L^6)Cl_3]$	10	15	12	9	9	13	17	15	16	14		15	16	16		NT	NT	15
$[Cu_2(L^6)(dp)_2]3Cl$	f	13	15	15	16	15	21	12	10	17		18	20	19		NT	NT	21
$CuCl_2 \cdot 2H_2O$	32	28	32	33	26	34	36	37	22	26	28	26	34	38	36			

*Inhibition zone (mm). X[a]: CFU[a]/mL (inoculum). The X[a] value is in the range 7.6×10^8-8.3×10^7 for the Gram-positive bacteria and 8.7×10^8-$9.6\times10^7$for the Gram-negative bacteria.

[a]Number of Colony Forming Units.

[b]Ampicillin (10 μg/disc). [c]Streptomycin (10 μg/disc).

[d]Nystatin 100 Units (10 μg/disc).

[e]Inhibition zone, mm.

[f]No inhibition zone is determined. Blanks mean not investigated. NT: Not tested.

1: *Corynebacterium xerosis*, 2: *Bacillus brevis*, 3: *Bacillus megaterium*, 4: *Bacillus cereus*, 5: *Mycobacterium smegmatis*, 6: *Staphylococcus aureus*, 7: *Micrococcus luteus*, 8: *Enterococcus faecalis*. 1′: *Pseudomonas aeruginosa*, 2′: *Klebsiella pneumoniae*, 3′: *Escherichia coli*, 4′: *Yersinia enterocolitica*, 5′: *Kluyveromyces fragilis*, 6′: *Saccharomyces cerevisiae*, 7′: *Candida albicans*.

group (>C=N) with the active centers of the cell constituents resulting in the interference with normal cell process.

In order to investigate the state of the chloride ions in the complexes, the thermal properties of the complexes have been studied using the t.g. and d.t.a techniques in the temperature range 20–1000 °C. All complexes decompose to the oxide in three steps, and they have similar properties. Moreover, the thermal stability of the homodinuclear and mixed-ligand Cu^{II} complexes have been compared. In the $[Cu(L^n)Cl_3]$ complexes, as the chloride ions coordinated to the copper ions, in the t.g. curve, the chloride ions have been lost in the 300–350 °C temperature range. But, in the mixed-ligand Cu^{II} complexes, the chloride ion loss from the complex is in the 185–220 °C temperature range. This situation is seen in Figure 8: the curve of the complex $[Cu(L^1)(dp)_2]Cl$. Figure 8 confirms that the chloride ion did not coordinate to the Cu^{II} ions. Another important feature, the mixed-ligand

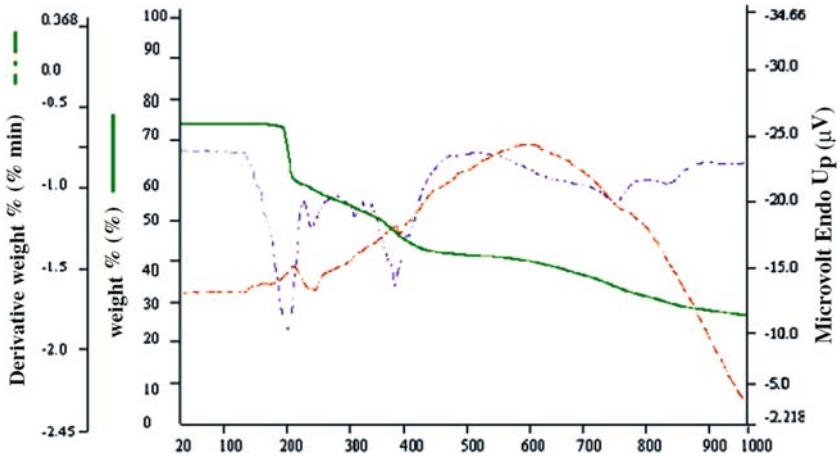


Fig. 8. The thermal curves of the complex $[Cu(L^1)(dp)_2]Cl$.

complexes have lower thermal stability than the other complexes. This may be due to the steric effects between the 2,2′-dipyridyl ligands in the complexes. In the higher temperatures, all complexes decompose to the metal oxide.

Acknowledgement

The present study was financially supported by K.Maras Sutcu Imam University, Head of Research Unit (Project code: 2004/4–5).

References

1. N. Oishi, Y. Nishida, K. Ida and S. Kida, *Bull. Chem. Soc. Jpn.*, **53**, 2847 (1980).
2. U. Casellato, S. Tamburini, P.A. Vigato, A. de Stefani, M. Vidali and D.E. Fenton, *Inorg. Chim. Acta*, **69**, 45 (1983).
3. M.R. Malachowski and M.G. Davidson, *Inorg. Chim. Acta*, **162**, 199 (1989).
4. K.D. Karlin, Y. Gultneh, T. Nicholson and J. Zubieta, *Inorg. Chem.*, **24**, 3727 (1985).
5. M.R. Malachowski, H.B. Huynh, L.J. Tomlinson, R.S. Kelly and J.W. Furbee, *J. Chem. Soc. Dalton. Trans.*, **31**, 31 (1995).
6. F. Zippel, F. Ahlers, R. Werner, W. Haase, H.-F. Nolting and B. Krebs, *Inorg. Chem.*, **35**, 3409 (1996).
7. J. Haggin, *Chem. Eng. News*, **71**, 23 (1993).
8. W. Kaim and J. Rall, *Angew. Chem.*, **108**, 47 (1996).
9. K.A. Magnus, H. Ton-That and J.E. Carpenter, *Chem. Rev.*, **94**, 727 (1994).
10. (a) T.B. Freedman, J.S. Loehr, T.M. Loehr, *J. Am. Chem. Soc.* **98**, 2809 (1976). (b) J.A. Larrabee, T.G. Spiro, N.S. Ferris, W.H. Woodruff, W.A. Maltese, M.S. Kerr, J. Am. Chem. Soc., 99, 1979 (1977). (c) J.A. Larrabee, T.G. Spiro, *J. Am. Chem. Soc.*, **102**, 4217 (1980). (d) J. Ling, L.P. Nestor, R.S. Czernuszewicz, T.G. Spiro, R. Fraczkiewicz, K.D. Sharma, T.M. Loehr, J. Sanders-Loehr, *J. Am. Chem. Soc.*, **116**, 7682 (1994).
11. (a) K.L. Lerch, *Life Chem. Rep.*, **5**, (1987) 221. (b) H.S. Mason, W.L. Fowlks, E. Peterson, *J. Am. Chem. Soc.*, **77**, 2914 (1955).
12. M. Tre'molie'res and J.B. Bieth, *Phytochemistry*, **23**, 501 (1984).
13. D. Meiwes, B. Ross, M. Kiesshauer, K. Cammann, H. Witzel, M. Knoll, M. Borchardt and C. Sandermaier, *Lab. Med.*, **15**, 24 (1992).
14. F. Koseoglu, E. Kılıç and D. Uysal, *Talanta*, **42**(12), 1875 (1995).
15. M. Dolaz, M. Tümer and M. Dıgrak, *Transition Met. Chem.*, **29**, 528 (2004).
16. G.H. Jeffery, J. Basset, J. Mendham, and R.C. Denny, Vogel's Quantitative Chemical Analysis, 5th Edit., Longmand Scientific and Technical Ltd., Essex (U.K.), 1989, p. 447.
17. C.H. Collins, P.M. Lyne and J.M. Grange, *Microbiological Methods*, Butterworths & Co. Ltd., London, 1989.
18. G. Gran, *Acta Chem. Scand.*, **4**, 559 (1950).
19. F.J.C. Rossotti and H.J. Rossotti, *Chem. Educ.*, **42**, 375 (1965).
20. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
21. A. Gölcü, M. Tümer, H. Demirelli and A.R. Wheatly, *Inorganic. Chim. Acta*, **358**, 1785 (2005).
22. M. Tümer, C. Çelik, H. Köksal and S. Serin, *Transition Met. Chem.*, **24**, 525 (1999).
23. M. Tümer, H. Köksal, S. Serin and M. Dığrak, *Transition Met. Chem.*, **24**, 13 (1999).
24. M. Tümer, H. Köksal, M.K. Şener and S. Serin, *Transition Met. Chem.*, **24**, 414 (1999).
25. M. Tümer, B. Erdoğan, H. Köksal, S. Serin and M.Y. Nutku, *Synth. React. Inorg. Met-Org. Chem.*, **28**, 529 (1998).
26. H. Köksal, M. Tümer and S. Serin, *Synth. React. Inorg. Met.-Org. Chem.*, **26**, 1577 (1996).
27. M. Tümer, H. Köksal and S. Serin, *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 775 (1997).
28. M.R. Malachowski, M.G. Davidson and J.N. Hoffman, *Inorg. Chim. Acta*, **157**, 91 (1989).
29. B.G. Tweedy, *Phytopathology*, **25**, 910 (1964).