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The Preparation of Binuclear Complexes and their Catalytic Behaviour in the Oxidation of 3,5-di-t-butylcatechol

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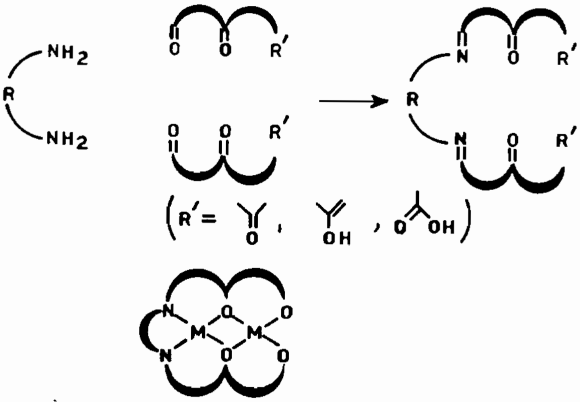
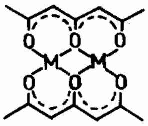
The complexes of type $M(HL)_2nH_2O$ ($n = 0, 1, 2$; $M = Cu^{2+}$, Ni^{2+}, Co^{2+}, Mn^{2+}, TiO^{2+}, Pd^{2+}; H_2L = β,δ-triketones or β-ketophenols) have been prepared and characterized by elemental analyses and physico-chemical measurements. These mononuclear compounds were used as ligands to prepare homo- and heterobinuclear complexes. Magnetic moments and spectral data are reported. The copper(II) homodinuclear complexes have been tested as catalysts in the oxidation of 3,5-di-t-butylcatechol.

Introduction

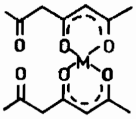
Diamine Schiff base derivatives of 1,3,5-triketones have been shown to be capable of binding two different metal ions within the same molecules giving a series of heterobinuclear complexes [1].

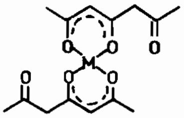


This is due to the different ligand field strengths of the two coordination sites, O_2O_2 and N_2O_2 respectively. β-triketones and the analogous β-ketophenols are also able to form binuclear complexes



but for these cases only homodinuclear complexes have so far been reported [2]. This is due to the difficulty in obtaining temperature stable mononuclear complexes, since they by heating transform into homodinuclear compounds. We have reacted the ligands (2,4,6-heptanetrione (H_2daa), *o*-acetylacetophenol (H_2aap) and 2-benzoylacetophenol (H_2bap) with metal salts in the presence of sodium acetate or LiOH and we have obtained the mononuclear complexes:





Using some of these complexes as ligands towards a second metal ion we were able to prepare heterodinuclear complexes and to study their physico-chemical properties.

By considering also that copper(II)-containing proteins can catalyse the oxidation of some organic substrates, we have tested the homodinuclear complexes of copper(II) as catalysts in the oxidation of 3,5-di-t-butylcatechol to quinone, and this paper reports the preliminary results of this investigation.

Experimental

The ligands 2,4,6-heptanetrione (H_2daa), *o*-acetoacetylphenol (H_2aap) and 2-benzoylacetophenol (H_2bap) were prepared according to literature procedures [3–5]. Their purity was established by elemental analyses, infrared and ^{1}H NMR spectra.

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Preparation of Mononuclear Complexes

The preparations of the cobalt(II) and manganese(II) complexes were carried out under nitrogen atmosphere, while for the other complexes the reactions were carried out in air.

Preparation of M(Hbap)$_2$. M = Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+})

A solution of the ligand (2 mmol) in MeOH was treated with LiOH (2 mmol) dissolved in water (10 ml). The solution was stirred for 30 min. The appropriate metal acetate (1 mmol) in MeOH was then added and the solution was stirred for 5 h at room temperature. The solid formed was filtered, washed with methanol and water and dried under vacuum.

Table I summarizes elemental analyses, magnetic and spectral data of these complexes.

Preparation of M(Haap)$_2$. (M = Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+})

To the ligand dissolved in acetone a water solution of the appropriate metal acetate was added. The mixture was stirred for 30 min and then treated with sodium acetate (1 mmol). The mixture was stirred at room temperature for 5 h. The precipitate was collected by filtration, washed with water and acetone and dried under vacuum.

Preparation of TiO(HL)$_2$. HL = Hbap, Haap, Hdaa)

To a benzene solution of the ligand (1 mmol), deaerated by bubbling N_2, Ti(i-propoxide)$_4$ (5 mmol) was added. The resulting solution, after stirring at room temperature for 5 h, was concentrated at room temperature under vacuum to 20 ml and treated with n-pentane (50 ml). The resulting yellow precipitate was filtered, washed with benzene/n-pentane 1:4 and dried under vacuum. Analysis data and magnetic and spectral properties are reported in Tables I and III.

Preparation of Pd(Hdaa)$_2$

To a water suspension of the ligand (2 mmol), LiOH (2 mmol) was added. The resulting solution was stirred for 30 min and then $PdCl_2$ (1 mmol) in water (50 ml) was added. A yellow precipitate

TABLE I. Physical and Analytical Data for the Prepared Chelates (Melting points 270 °C).

Complex	C		H		Metal	
	calc.	found	calc.	found	calc.	found
$Cu(Hbap)_2$	66.48	66.75	4.06	4.35	11.73	9.92
$Ni(Hbap)_2 \cdot 2H_2O$	62.82	62.33	4.53	5.23	–	–
$Co(Hbap)_2 \cdot 2H_2O$	62.82	63.40	4.33	4.95	10.29	9.35
$Mn(Hbap)_2 \cdot 2H_2O$	63.26	64.20	4.56	4.17	–	–
$Cu_2(bap)_2$	59.60	60.11	3.31	3.36	–	–
$Ni_2(bap)_2 \cdot 4H_2O$	54.05	54.30	4.20	3.72	–	–
$Co_2(bap)_2 \cdot 4H_2O$	54.05	54.90	4.20	3.87	17.71	16.92
$Pd_2(bap)_2$	52.24	52.76	2.90	3.20	–	–
$CoCu(bap)_2 \cdot 2H_2O$	56.73	57.10	3.78	3.48	10.01	10.88
$NiCu(bap)_2 \cdot 2H_2O$	56.73	56.80	3.78	3.72	10.01	10.88
$TiO(Hbap)_2 \cdot H_2O$	64.28	64.50	4.28	4.70	–	–
$TiO(Hdaa)_2 \cdot H_2O$	46.15	46.40	5.49	4.85	–	–
$Pd(Hdaa)_2$	43.25	42.96	4.63	4.25	–	–
$Cu(Hdaa)_2$	48.62	49.10	5.21	5.30	18.39	18.10
$Ni(Hdaa)_2 \cdot 2H_2O$	44.56	45.10	5.83	5.97	–	–
$CuTiO(daa)_2 \cdot H_2O$	39.48	39.60	4.23	4.30	14.93	15.20
$CuPd(daa)_2$	37.41	36.83	3.56	3.40	12.73	11.97
$Cu_2(daa)_2$	36.92	36.75	4.33	4.52	39.06	39.03
$Cu(Haap)_2$	57.48	57.80	4.31	4.49	15.21	15.32
$Ni(Haap)_2 \cdot 2H_2O$	53.45	52.34	4.89	5.25	–	–
$Co(Haap)_2 \cdot 2H_2O$	53.45	53.28	4.89	4.65	13.14	12.90
$Mn(Haap)_2 \cdot 2H_2O$	53.93	54.52	4.94	4.96	–	–
$Cu_2(aap)_2$	50.10	50.27	3.34	3.40	26.53	25.87
$Co_2(aap)_2 \cdot 4H_2O$	44.28	44.38	4.42	4.10	21.77	21.05
$Ni_2(aap)_2 \cdot 4H_2O$	44.28	44.88	4.42	4.06	–	–
$NICu(aap)_2 \cdot 2H_2O$	47.01	47.21	3.91	3.88	12.44	12.48
$TiO(Haap)_2 \cdot H_2O$	55.04	54.83	4.58	4.70	–	–
$Pd_2(aap)_2$	45.97	45.80	3.06	2.80	–	–

formed immediately, which after stirring for 3 h, was filtered and dissolved in $CHCl_3$. The solution was passed through a filter of cellulose to eliminate metallic Pd and was evaporated to dryness. The residue was washed with a little chloroform and dried in vacuo.

Preparation of Binuclear Complexes

Preparation of $Pd_2(L)_2$. (L = Hbap, Haap)

To a water solution of the ligand (2 mmol) and LiOH (4 mmol) $PdCl_2$ (2 mmol) in water (50 ml) was added. A yellow precipitate appeared and stirring was continued for 3 h. The solid was filtered, washed with water and dissolved in $CHCl_3$. The solution, clarified by passing through a cellulose column, was evaporated to dryness. The residue was washed with a little chloroform and dried in vacuo.

Preparation of Homobinuclear Chelates

Two general methods have been employed:

A) To a solution of the mononuclear chelate (1 mmol) in pyridine (50 ml), a methanolic solution of the corresponding metal acetate (1 mmol) and LiOH (2 mmol) was added. The solution was heated to 50 °C for 3 h, then evaporated to dryness and treated with MeOH. The resulting precipitate was filtered, washed with a pyridine/methanol solution and dried in vacuo.

B) A hot methanolic solution of metal acetate (2 mmol) was added to a solution containing 2 mmol of the ligands in 100 ml of MeOH and 4 mmol of LiOH in 5 ml of H_2O. The resulting mixture was heated at 50 °C for 3 h, the precipitate was filtered, washed with methanol and water and dried in vacuo.

Preparation of Heterobinuclear Chelates

To a pyridine solution (30 ml) of the mononuclear complex (1 mmol) at 40 °C a methanolic solution of the appropriate metal acetate (1 mmol), was added, after 15 min, LiOH (2 mmol) dissolved in little H_2O. The solution was stirred for 3 h at 50 °C and then evaporated to dryness. The residue was treated with methanol, filtered, washed with a pyridine/methanol solution and dried in vacuo.

Oxidation Reaction of 3,5-Diterbutylcatechol by O_2

A chloroform solution of 3,5-DTBC was added to a solution of the complex in pyridine. The resulting solution was kept at 17 °C in a open flask for 6–7 h. The presence of the quinone formed (3,5-DTBCQ) was determined by thin layer chromatography over silica gel plates, eluting with $CHCl_3$/n-exane (3:1). The yield of quinone was determined by measurements of the absorption spectra of the resulting solution. 3,5-DTBCQ has a characteristic absorption band at 400 nm in $CHCl_3$/py solution.

Results and Discussion

There are several research fields in which it would be advantageous to have a variety of well characterized mixed metal complexes. These fields include physico-chemical studies such as antiferromagnetic coupling, the development of unusual homogeneous catalysts and the design of compounds with unusual properties. Clearly, the first problem is associated with the preparation of pure compounds and the second is to develop a systematic synthetic procedure so that many pure heterodinuclear complexes may be prepared. We have developed a synthetic prodedure to prepare this type of complexes, which proceeds in a stepwise fashion:

a) a binucleating ligand is used which has available two different coordination sites,

b) the preparation of pure and well characterized mononuclear chelates is carried out, and

c) the reaction of the mononuclear compounds with the required metal salt to obtain heterobinuclear compounds.

In this work we have tried to extend this procedure to the preparation of heterobinuclear complexes with β,δ-triketones and β-ketophenols, for which there are no previous reports. This is due to the difficulties in isolating mononuclear precursors; in fact in solution, at ambient temperatures, they readily give homobinuclear complexes according to the reaction:

$$2M(HL)_2 \rightarrow M_2L_2 + 2HL$$

Mononuclear Chelates

Our first aim was therefore to determine the best reaction conditions for the preparation of mononuclear compounds. In Table II we report a series of reaction conditions and the obtainable products for reactions concerning copper(II).

From the data reported in Table II it can be stated that the temperature is an influential parameter in the preparation of mononuclear complexes. The reaction of metal acetates with the β-ketophenols at room temperature in 1:2 molar ratio in the presence of LiOH or sodium acetate gives mononuclear complexes, as does the reaction of Ti^{4+} or Pd^{2+} with H_2daa under the same conditions. In contrast, H_2daa yields only the dinuclear complexes of copper(II) and nickel(II) when the metal acetates are reacted with the ligand, even in a large excess (4 fold) at room temperature. The formation of mononuclear complexes of copper(II) and nickel(II) results only at 0 °C.

The elemental analyses suggest that the molecular formula for these complexes is $M(HL)_2(H_2O)_n$ ($M = Pd^{2+}$, $n = 0$; $M = Cu^{2+}$, TiO^{2+}, $n = 0$; $M = Co^{2+}$, Ni^{2+}, Mn^{2+}, $n = 2$).

TABLE II. Experimental Conditions for the Reaction between Cu(acetate)$_2$ and the β,δ-Triketones and β-Ketophenols Ligands.

Solvent	Temperature	Base	Products
MeOH	25 °C	LiOH	$Cu(Hbap)_2$, $Cu(Haap)_2$, $Cu_2(daa)_2$
MeOH	25 °C	NaOAc	$Cu(Hbap)_2$, $Cu(Haap)_2$, $Cu_2(daa)_2$
MeOH	0 °C	LiOH/NaOAc	$Cu(HL)_2$(L = Hbap, Haap, Hdaa)
MeOH	0 °C	–	$Cu(HL)_2$(L = Hbap, Haap, Hdaa)
MeOH	25 °C	–	$Cu(Hbap)_2$, $Cu(Haap)_2$, $Cu_2(daa)$
Acetone	25 °C	LiOH or NaOAc	$Cu(Hbap)_2$, $Cu(Haap)_2$, $Cu_2(daa)$
Acetone	0 °C	LiOH or NaOAc	$Cu(HL)_2$

The mononuclear chelates can be converted, by heating, into the homobinuclear chelates; the maximum temperature below which the mononuclear complexes are stable, in pyridine or ethanol, is 50 °C for $M(Hbap)_2$ and $M(Haap)_2$ (M = Cu, Ni, Co, Mn) and 0 °C for the $Ni(Hdaa)_2$ and $Cu(Hdaa)_2$ complexes.

The infrared spectra of the H_2daa chelates show a free carbonyl band at about 1720 cm^{-1} and a multiplet band in the region 1660–1500 cm^{-1} due to a coordinated carbonyl and to the olefinic group involved in the chelate ring. The IR spectra of β-ketophenolic chelates do not show bands due to the free carbonyl group, but a multiplet in the same region as $M(Hdaa)_2$ chelates and as found also in other β-diketonates [6, 7]. The highest absorption band, occurring near 1600 cm^{-1} in the infrared spectra of all the complexes, can be attributed to one of the C=O stretching modes of the chelate ring. The frequency assignment of the C=C modes is not simple; it was associated with a band near 1525 cm^{-1} in the spectra of β-diketonates and accordingly we have assigned a band, present in our spectra, at about 1510 cm^{-1} to C=C modes [8, 9]. It may be observed that the C=O stretching frequency for the transition metal complexes is:

$\mathrm{Pd} > \mathrm{Cu} > \mathrm{Ni}$

and this frequency decrease follows the Irving-Williams stability [10].

The TiO^{2+} complexes show, in addition to the bands reported above, a broad band near 800 cm^{-1}, due to the stretching of the TiO group. The lack of an intense band in the 1000 cm^{-1} region shows the absence of terminal Ti=O stretching modes. We thus assume that, in view of the dimeric nature of $TiO(HL)_2$ in the solid state, this species may contain $\mathrm{Ti}\genfrac{}{}{0pt}{}{/O\backslash}{\backslash O/}\mathrm{Ti}$ units as found for $TiO(acac)_2$ [11].

The electronic spectra in dmso solution show bands in the UV region due to the internal transition of the ligands and d–d bands in the visible region (Table III).

The spectra of the cobalt(II) complexes are almost identical to each other, exhibiting a low intensity band at *ca.* 1150 nm and two bands at 570 and 500 nm; these features are typical for a weak octahedral field and the magnetic data are of the same order as those commonly found for high spin octahedral cobalt(II) complexes.

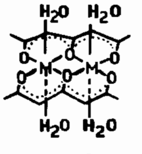
The room temperature magnetic moments of nickel(II) complexes are in the range normally found for octahedral coordinated nickel(II) complexes. Their electronic spectra are identical to each other and show three absorption bands between 500 and 1300 cm^{-1}, as expected for octahedral complexes. The magnetic properties of the copper(II) complexes with the ligands H_2daa, H_2bap and H_2aap closely resemble those of $Cu(acac)_2$ [12], suggesting that the former complexes exist as planar molecules; the d–d absorption bands are those expected for a square planar copper(II) β-diketonato complex.

The spectra of the manganese(II) complexes show only the broad band at *ca.* 500 nm common to high spin octahedral manganese(II) complexes, since all transitions are both spin and symmetry forbidden. Magnetic susceptibility measurements ($Mn(Haap)_2$-μ_{eff} = 5.87 BM; $Mn(Hbap)_2\mu_{eff}$ = 5.90 BM) agree with the proposed geometry.

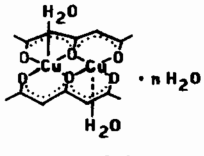
In the absence of X-ray structural information it has not been possible to identify the nature of the mononuclear species, *i.e.* which of the isomeric forms is present.

Homobinuclear Chelates

These complexes can be obtained by reaction of the ligands with the appropriate metal salt or by reaction of mononuclear complexes with metal acetate; they can also be prepared by heating the mononuclear analogues as reported above. Their electronic and infrared data suggest that these complexes are of the type:



M = Cu^{2+}, Ni^{2+}



n = 0,2

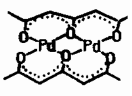


TABLE III. Spectroscopic Data and Magnetic Moments (BM) of the Prepared Complexes.

Complex	IR (cm^{-1}) Frequency in the 1650–1500 cm^{-1} range				UV (nm)					μ(B.M)[a]
$Cu(Hbap)_2$	1610	1585	1520		300	340	–	670	–	1.73
$Ni(Hbap)_2 \cdot 2H_2O$	1610	1590	1510		–	–	370	640	1100	2.91
$Co(Hbap)_2 \cdot 2H_2O$	1610	1590	1510		–	–	370	620	–	4.64
$Mn(Hbap)_2 \cdot 2H_2O$	1610	1590	1510		–	–	380	–	–	–
$TiO(Hbap)_2 \cdot H_2O$[b]	1610	1580	1530		320	–	–	–	–	–
$Cu_2(bap)_2$	–	1590	1510		300	330	370	670	–	1.43
$Ni_2(bap)_2 \cdot 4H_2O$	–	1580	1520		–	345	–	655	1098	3.80
$Co_2(bap)_2 \cdot 4H_2O$	–	1590	1510		–	–	370	620	–	6.48
$Pd_2(bap)_2$	1610	1580	1510		250	320	370	–	–	diam
$CoCu(bap)_2 \cdot 2H_2O$	1610	1590	1520		300	–	370	600	670	4.60
$NiCu(bap)_2 \cdot 2H_2O$	1610	1590	1510		–	340	370	610	670 1100	2.32
$Cu(Hdaa)_2$	1720	1620	1580	1530		320	650			1.75
$Ni(Hdaa)_2 \cdot 2H_2O$	1718	1610	1570	1540		320	630		1100	3.31
$Pd(Hdaa)_2$	1715	–	1550	1520		320	–	–	–	diam
$TiO(Hdaa)_2 \cdot H_2O$[c]	1715	–	1590	1520		320	–	–	–	diam
$TiOCu(daa)_2 \cdot H_2O$[d]	–	–	1590	1520		320	660	–	–	1.77
$PdCu(daa)_2$	–	–	1590	1520		310	670	–	–	1.80
$Cu(Haap)_2$	1615	1590	1560		340	370	680	–	–	1.78
$Ni(Haap)_2 \cdot 2H_2O$	1612	1585	1490		225	342	655	1100		3.23
$Co(Haap)_2 \cdot 2H_2O$	1610	1585	1510		–	360	600	–		4.98
$Mn(Haap)_2 \cdot 2H_2O$	1610	1588	1510		315	330	–	–		–
$TiO(Haap)_2 \cdot H_2O$[e]	1610	1595	1550		325	–	–	–		–
$Cu_2(aap)_2$	–	1589	1560		300	380	–	–		1.40
$Co_2(aap)_2 \cdot 4H_2O$	1600	1570	1510		–	360	600	–		6.50
$Ni_2(aap)_2 \cdot 4H_2O$	1612	1535	1510		–	350	650	1110		3.75
$Pd_2(aap)_2$	1610	1575	1510		260	315	–	–		diam
$NiCu(aap)_2 \cdot 2H_2O$	1610	1585	1500		–	–	690	1100		2.39

[a] The magnetic values are for the whole molecule. [b] ν(Ti–O) is at 805 cm^{-1}. [c] ν(Ti–O) is at 800 cm^{-1}. [d] ν(Ti–O) is at 810 cm^{-1}. [e] ν(Ti–O) is at 805 cm^{-1}.

The IR spectra show bands in the region 1600–1500 cm^{-1} which are typical of coordinated carbonyl groups and ethylenic bonds. The presence of water in these complexes is confirmed by a broad band ranging from 3600 to 3000 cm^{-1}, due to the stretching modes of the coordinated water.

The electronic spectra of copper(II) chelates in dmso solution is as expected for copper(II) ethylacetonate or hydroxyacetophenonate complexes.

There is a broad band at about 670 nm, due to the d–d transitions. The nickel(II) compounds show a very broad band at 1100 cm^{-1} and a second broad band or shoulder in the region 660–600 cm^{-1}, similar to those found for some nickel(II) diketonate complexes [12].

The electronic spectra of the cobalt(II) compounds closely resemble previously reported results for $Co(acac)_2(py)_2$ [13, 14] and are consistent with an octahedral coordination. The magnetic moments of dinuclear complexes are lower than the spin only value (Table III), similar to those obtained for analogous adducts in which an antiferromagnetic coupling is operative [15–17].

Heterobinuclear Chelates

These complexes can be obtained by reaction of stable mononuclear chelates with the appropriate metal acetate; however it is necessary to pay attention to the temperature reaction, since the mononuclear chelates can be converted into the 2:2 ones by heating above 50 °C. It was impossible to prepare heterodinuclear complexes of the ligands H_2daa using as starting material $Cu(Haap)_2$, $Cu(Hdaa)_2$ or $Ni(Hdaa)_2$ since, at the experimental temperature, these complexes transform into homobinuclear chelates. $Cu(Hbap)_2$, $Ni(Haap)_2$, $Pd(Hdaa)_2$, $TiO(Hdaa)_2$ were therefore chosen to prepare heterodinuclear chelates for the following reasons:

i) the compounds are easily prepared in good

yields and high purity,
and

ii) under the preparative conditions used, they do not transform into homodinuclear chelates.

Their infrared data (Table III) have essentially the same shape as the corresponding homobinuclear complexes. The strong band in the 1585–1600 cm^{-1} region may be associated with the coordinated carbonyl groups, and the band in the 1500–1530 cm^{-1} region corresponds to the C=C vibration.

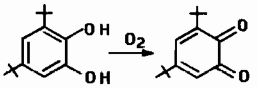
The electronic spectra in dmso solution show, in addition to bands in the UV region due to internal transition in the ligand, the d–d bands of the transition ions.

The magnetic properties of $CuPd(daa)_2$ and $TiOCu(daa)_2$ are explained assuming that the entire paramagnetism arises from the copper(II) ion, on this basis the magnetic properties are those expected for isolated d^9 copper(II) ion. The room temperature magnetic moments of $CoCu(bap)_2 2H_2O$ (μ_{eff} = 4.60 BM), $NiCu(bap)_2 2H_2O$ (μ_{eff} = 2.33 BM) and $NiCu(aap)_2 \cdot 2H_2O$ (μ_{eff} = 2.39 BM) are lower than the spin only values and similar to those found for analogous complexes in which a magnetic coupling is present.

Oxidation Tests

It is known that copper(II) containing proteins catalyse, for example, the oxidation of dihydroxy phenols and ascorbate with associated four electron reduction of oxygen to water. These enzymes contain three distinct types of copper(II) atoms termed Type 1, 2 and 3 [18]. Type 1 and 2 copper(II) ions are paramagnetic, magnetically diluted, and operate as mononulcear chelates. For type 3 a binuclear structure has been proposed [19]. Although much progress has been made by studying the kinetics of oxidations of substrates and reduction of the O_2 by laccase [20] and ceruloplasmin [19, 20], the search continues for model systems which imitate the special structural and catalytic properties of these enzymes.

We have examined the catalytic activity of some dinuclear copper(II) complexes for oxidation of 3,5-butylcatechol by O_2 to quinone according to the reaction:



The activity of binuclear copper(II) complexes was followed by optical spectrometry using a modification of the method of Lintvedt [21]. 3,5-DTBC shows a characteristic absorption band at 400 nm, which can be a good measure for the catalytic activity of copper(II) ions in the oxidation of 3,5-DTBC. Figure 1 shows the growth of 3,5-DTBQ with time in the oxidation reaction with $Cu_2(aap)_2$ as the catalyst.

Figure 2 compares the oxidation of 3,5-DTBC by $Cu_2(aap)_2$ in dioxygen, air and dinitrogen atmospheres after the same time interval has elapsed. The complex has little activity under a dinitrogen atmosphere while it acts as a catalyst in both dioxygen and air with a small increase in activity on going from air to a pure dioxygen atmosphere.

A comparison of the activity in a group of homobinuclear complexes is shown in Fig. 3 and a further comparison between mononuclear and binuclear species is given in Fig. 4. Our results indicate that for the binuclear complexes the activity series is:

$$Cu_2(aap)_2 > Cu_2(bap)_2 > Cu_2(daa)_2 > Cu_2(baa)_2$$

and that the binuclear complexes show an enhanced activity over the mononuclear complexes. In a related series of experiments using a wide range of copper(II) complexes Kida [22] found that square coplanar species did not activate the oxidation and this suggests that for our systems the mononuclear chelates, in solution (pyridine/$CHCl_3$) could possess a non planar structure, possibly being pentacoordinated with a molecule of pyridine in the fifth position.

The oxidation rate of DTBC, using binuclear copper(II) complexes as catalysts, is lowered by the presence of DTBQ. A plausible explanation of these experimental results is that the electron transfer from catechol to the copper(II) complex begins after the formation of an intermediate of the type $Cu_2(L)_2(DTBC)$ (L = triketones or β-ketophenols) which could be prevented by the competitive formation of $Cu_2(L)_2(DTBQ)$ complex.

The binuclear cobalt(II) complexes also showed a catalytic oxidation of 3,5-DTBC (Figs. 4 and 5). However in contrast to the mononuclear copper(II) complexes the mononuclear cobalt(III) complexes, such as $Co(Haap)_2 \cdot 2H_2O$, $Co(Hbap)_2 \cdot 2H_2O$ showed little or no catalytic activity.

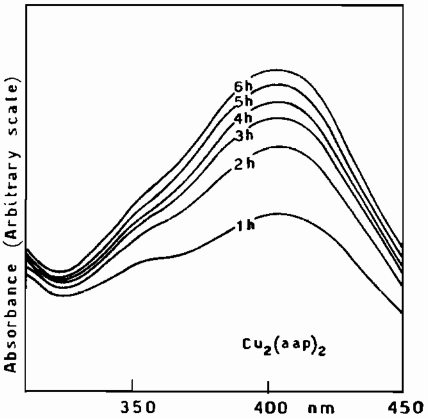


Fig. 1. Oxidation of 3,5-DTBC by $Cu_2(aap)_2$.

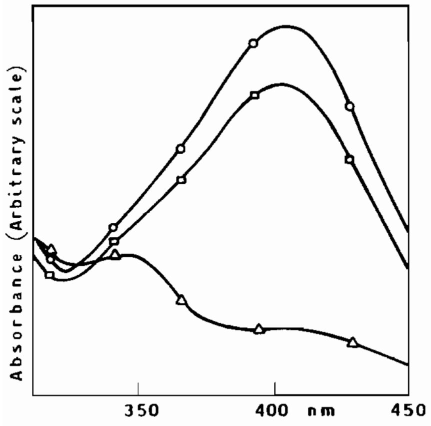


Fig. 2. The oxidation of 3,5-DTBC by $Cu_2(aap)_2$ in different atmospheres after the same time interval (6 h); ○ $Cu_2(aap)_2$ with O_2; □ $Cu_2(aap)_2$ in air; △ $Cu_2(aap)_2$ in N_2 atmosphere.

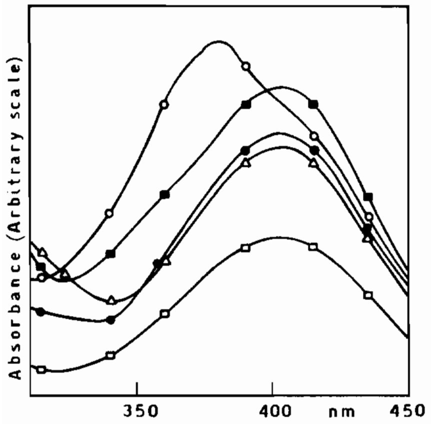


Fig. 3. A comparison of the oxidation of 3,5-DTBC by different complexes after 6 h; ○ $Cu_2(bap)_2$; ■ $Cu_2(aap)_2$; ● $Cu_2(daa)_2$; □ bis(benzoylacetonate)copper(II); △ Cu_2-$(bap)_2(MeOH)_2$.

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References

1 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, Chem. Soc. Rev., 8, 199 (1979).
2 P. A. Vigato, U. Casellato, S. Tamburini, F. Milani and M. M. Musiani, *Inorg. Chim. Acta.*, *61*, 89 (1982).
3 J. R. Bethel and P. Maitland, *J. Chem. Soc.*, 3751 (1962).
4 G. Wittig, *Ann. Chem.*, *446*, 173 (1926).
5 T. S. Wheeler, *Org. Syn. Coll. Vol.*, *4*, 479 (1963).

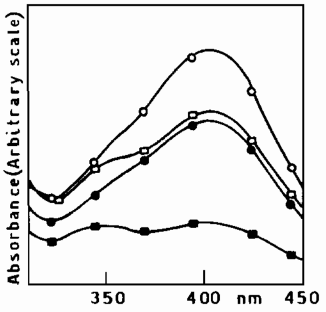

Fig. 4. The oxidation of 3,5-DTBC by mono and binuclear complexes (after 6 h); ○ $Cu_2(aap)_2$; □ $Cu(Haap)_2$; ● Co_2-$(aap)_2$; ■ $Co(Haap)_2$.

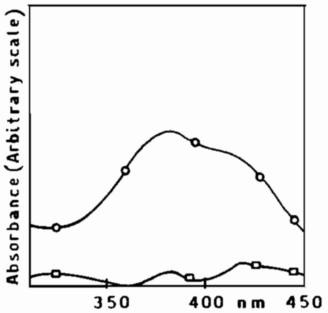

Fig. 5. The oxidation of 3,5-DTBC by mono and binuclear complexes (after 6 h); ○ $Co_2(bap)_2$; □ $Co(Hbap)_2$.

6 H. Musso and H. Junge, *Tetrahedron Letters, 33* 4003 (1966).
7 S. Pinchas, B. L. Silver and I. Laulicht, *J. Chem. Phys.*, *46*, 1506 (1967).
8 G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, *7*, 330 (1968).
9 M. Mikani, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, 23A*, 1129 (1967).
10 H. J. H. Irving and R. J. P. Williams, *Nature, 162*, 746 (1948).
11 I. R. Beattie and J. P. Fawcett, *J. Chem. Soc.*, *A*, 1583 (1967).
12 J. T. Hashagen and J. P. Fackler, jr., *J. Am. Chem. Soc.*, *87*, 2821 (1965).
13 S. Yamada, *Coord. Chem. Rev.*, *1*, 145 (1965).
14 R. H. Holm, G. W. Everet and A. Chakravorty, *Prog. Inorg. Chem.*, *7*, 83 (1966).
15 J. M. Kuszai, B. Tomlonovic, D. P. Murta, R. L. Lintvedt and M. D. Glick, *Inorg. Chem.*, *12*, 1297 (1973).
16 M. G. Haeg, J. L. Mack, M. D. Glick and R. L. Lintvedt, *Inorg. Chem.*, *20*, 833 (1981).
17 R. L. Lintvedt, L. L. Borer, J. P. Murta, J. M. Kuszai and M. D. Glick, *Inorg. Chem.*, *13*, 18 (1974).
18 R. Malkin and B. G. Malmstrom, *Adv. Enzymology, 33*, 177 (1970).
19 H. Beinert, *Coord. Chem. Rev.*, *33*, 55 (1980).
20 S. H. Laurie and E. S. Mohammed, *Coord. Chem. Rev.*, *33*, 279 (1980).
21 S. Tsuruya, R. L. Lintvedt, 'Abstracts of Papers, 176th National Meeting of the American Chemical Society, Miami, Sept. 1978.
22 N. Oishi, Y. Mishida, K. Ida and S. Kida, *Bull. Chem. Soc. Japan, 53*, 2847 (1980).