

Structure of copper 4-(dimethylamino)pyridine complexes and their catalytic activity in the oxidative coupling of 2,6-dimethylphenol

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STRUCTURE OF COPPER 4-(*N,N*-DIMETHYLAMINO)PYRIDINE COMPLEXES AND THEIR CATALYTIC ACTIVITY IN THE OXIDATIVE COUPLING OF 2,6-DIMETHYLPHENOL*

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Summary

The oxidative coupling of 2,6-dimethylphenol (DMP) by copper complexes of 4-(*N,N*-dimethylamino)pyridine (DMAP) has been studied. Catalytic experiments were carried out in which the DMAP-to-copper ratio and the amount and nature of the copper counter ions were varied. Supporting UV and EPR experiments were performed, and it was concluded that both dinuclear and mononuclear complexes are catalytically active, the mononuclear species being the more active. In solution both species are in equilibrium with one another. The mono/di ratio can be increased by addition of extra DMAP ligands. An excess of coordinating counter-ions increases the amount of dinuclear species. However, a few coordinating counter-ions are inevitable, and the catalytically most active species was found to be 'Cu(DMAP)₄Cl(OH)', the role of Cl⁻ probably being that of a bridging counter-ion promoting the formation of dinuclear Cu(I) complexes for the reoxidation step. The DMAP ligands are coordinated to Cu(II) through the pyridine N-atoms, as was determined by X-ray analysis. The Cu(II)DMAP complexes are catalytically active even without initial hydroxide addition. It is believed that the strongly basic DMAP ligands produce some hydroxide from traces of water present in the reaction medium. The species 'Cu(DMAP)₄Cl(OH)' proved to be able to produce relatively high molecular weight polyphenylene oxide (PPO) in short time and with good specificity (> 95%).

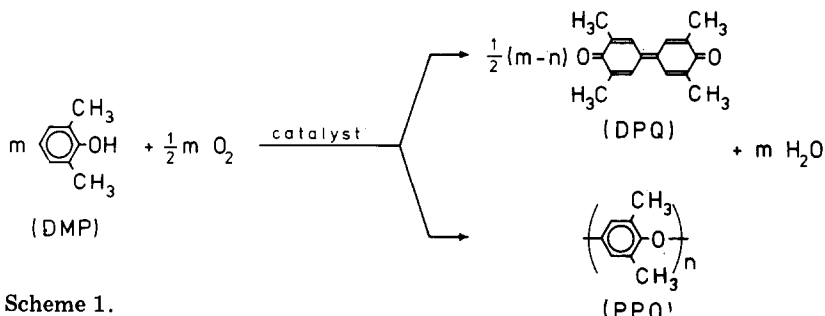
Introduction

It is well known that the oxidative coupling of 2,6-disubstituted phenols may proceed under mild reaction conditions if basic copper amine

*Dedicated to Prof. G. Manecke on the occasion of his 70th birthday.

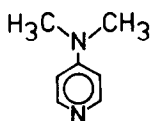
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complexes are used as catalysts. Depending on the reaction conditions and the size of the substituent groups R of the substrate, C—C coupling leading to the product diphenoquinone (DPQ)[†] or C—O coupling leading to the product polyphenylene oxide (PPO)^{††}, may be favoured. Especially when the substituent groups R are small, which is the case with 2,6-dimethylphenol (DMP), considerable amounts of the polymer PPO may be produced (Scheme 1).

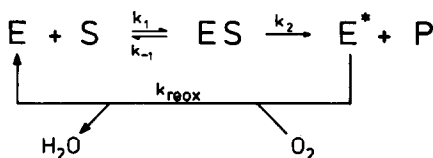


Scheme 1.

For the production of the engineering plastic PPO, an active catalyst with good specificity for PPO formation is needed. Verlaan *et al.* [1] discovered that copper complexes of 4-disubstituted aminopyridines fulfill these demands. Studies described in this paper are restricted to the ligand 4-(*N,N*-dimethylamino)pyridine (DMAP):



In general, the kinetics of the oxidative coupling of phenols with amine-copper catalysts can be described by the Michaelis-Menten concept for enzyme catalysis [2, 3] (Scheme 2).



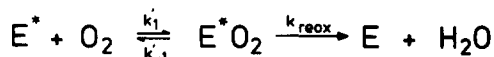
Scheme 2.

In Scheme 2, E stands for the Cu(II) complex, E^* for the Cu(I) complex, S for substrate, P for products and usually k_2 refers to the rate-determining step in the redox cycle. Verlaan *et al.* [1] found that this scheme is valid for polystyrene-bound DMAP ligands, and in that case real phenol oxidation

[†]DPQ = 4-(3,5-disubstituted-4-oxo-2,5-cyclohexadien-1-ylidene)-2,6-disubstituted-2,5-cyclohexadien-1-one.

^{††}PPO = poly-2,6-disubstituted-1,4-phenylene oxide.

rates are measured. For unbound DMAP, the dioxygen consumption was accelerated on raising the dioxygen pressure, indicating that reoxidation rates of Cu(I) to Cu(II) (k_{reox} in Scheme 2) are measured. Verlaan *et al.* showed that in this case Scheme 3 is valid, where k_{reox} is in fact rate determining.



Scheme 3.

Furthermore, it was found that, on raising the amine-to-copper ratio, the dioxygen consumption rate was enhanced and C—O coupling was favoured for both free and polystyrene-bound DMAP. This effect was attributed to an enhancement in basicity [4]. Finally, the reaction rate was found to be first-order in copper concentration.

Nowadays it seems likely that a general formula for the active copper complex for oxidative coupling of 2,6-disubstituted phenols can be given: $[Cu(OH)L_n]_m^+X_m^-$, where L = amine, X = Cl or Br and $1 \leq m \leq 4$. It has been suggested that the active complex is a dinuclear copper species ($m = 2$), bridged through two ligands. These ligands can be either two OH^- [5-7], or one X^- and one OH^- [8]. Schouten *et al.* [9] describe a complex with two Cl^- ions as bridging ligands, while this complex is decomposed by OH^- .

In this paper, experiments are described that were carried out to study whether or not the very basic DMAP ligands give catalytically active complexes with Cu(II), without initial addition of hydroxide ions. Furthermore, the influence of the nature of the counter-ions X in the complex on the catalytic activity and on the specificity for PPO production was investigated. Additional spectroscopic studies will attempt to elucidate these effects and to indicate the possible structure of the catalytically active species.

Experimental

Materials

1,2-Dichlorobenzene, as well as the copper salts $CuCl_2 \cdot 2H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$, were obtained from Merck as analytically pure grades. The copper salt $Cu(BF_4)_2 \cdot xH_2O$ ($x \sim 6$) was from Ventron GmbH. All copper salts were used as methanolic solutions with an exactly known (EDTA titration) copper concentration. Tetramethylammonium chloride was from Merck, as was methanol of Uvasol quality. 2,6-Dimethylphenol was from Aldrich and was purified by recrystallization from n-hexane. 4-(*N,N*-dimethylamino)pyridine was from Aldrich and used without further purification. The methanolic solution of tetramethylammonium hydroxide was from Fluka; KOH and LiOH were from Merck and analytically pure.

Oxidative coupling

The standard reaction conditions for oxidative coupling were: $T = 298.2$ K, $[\text{Cu}^{2+}] = 3.32 \times 10^{-3}$ mol dm⁻³, $[\text{DMP}] = 0.06$ mol dm⁻³, $P_{\text{O}_2} = 101.3$ kPa, total reaction volume = 0.015 dm³, shaking speed of reaction vessel = 4 - 5 Hz (high enough to prevent dioxygen diffusion from the gas phase to become rate-determining), solvent mixture 1,2-dichlorobenzene/methanol = 13/2 (vol.%). Hydroxide ions, if used, were added as methanolic lithium or potassium hydroxide or as tetramethylammonium hydroxide. The catalyst was prepared *in situ* by dissolving the desired copper salt and ligand (and optionally a hydroxide) in 1,2-dichlorobenzene/methanol. The cylindrical reaction vessel was connected to an automatic gas burette containing pure dioxygen. The reaction mixture was saturated with dioxygen and the oxidative coupling was started by addition of DMP. The vessel was violently shaken in a thermostatted bath, and the dioxygen consumption was recorded at constant pressure as a function of reaction time. The reaction rate R was calculated from the maximum slope of the dioxygen consumption curve, which was usually achieved within 10% of the total reaction-conversion.

Determination of catalytic specificity of the complexes and characterization of the produced PPO

For determination of catalytic specificity, some reactions were completed and aliquots of the reaction mixtures were diluted with solvent mixture. DPQ concentrations were determined with a PYE Unicam SP 8-200 UV/Vis spectrophotometer at 426 nm ($\epsilon = 61\,000$ dm³ mol⁻¹ cm⁻¹). From these data the percentage of DMP that had been transformed into DPQ could be calculated.

For characterization of produced PPO, an experiment with higher $[\text{DMP}]$ was carried out in order to obtain more polymer. The polymer was isolated at the end of the reaction by precipitation in an excess of acidified methanol. PPO was filtered, washed with methanol, dried under vacuum at 333 K, and an elemental analysis was carried out. $(\text{C}_8\text{H}_8\text{O})_n$; found (calculated): 78.9% C (80.0%) and 6.9% H (6.7%). The intrinsic viscosity, $[\eta]$, was determined with an Ubbelohde viscometer in chloroform at 298.2 ± 0.1 K.

Synthesis of copper DMAP compounds

Starting from the hydrated copper(II) salts (anions used were Cl^- , BF_4^- , NO_3^-) in MeOH as a solvent, addition of DMAP (in MeOH) in various molar ratios initially resulted in the following solid compounds: $\text{Cu}(\text{DMAP})_4(\text{BF}_4)_2$, $\text{Cu}(\text{DMAP})_4\text{Cl}_2$ and $\text{Cu}(\text{DMAP})_4(\text{NO}_3)_2$. All these compounds have been characterized by chemical analyses. Since the mixed solvent system MeOH/1,2-dichlorobenzene (2/13 v/v) had been used in the catalytic studies (*vide supra*), this solvent was also used in the case of CuCl_2 . Surprisingly, from this solvent system a number of other solid compounds could be isolated, *i.e.* $\text{Cu}_4\text{OCl}_6(\text{DMAP})_4$, $\text{CuCl}_2(\text{DMAP})_4(1,2\text{-dichlorobenzene})_2$ and $\text{CuCl}_2(\text{DMAP})_4(\text{H}_2\text{O})_2$. These products have also been

characterized by chemical analyses. The first compound might be formed through reaction of $\text{Cu}(\text{DMAP})_n\text{Cl}_2$ with hydration water in a basic medium [10]. However, the fact that such compounds can be isolated in the solid state does not necessarily mean that such species are also present as catalyst in solution. To obtain further information, spectroscopic measurements (EPR and UV-Vis) were also performed on solutions.

Physical measurements and analysis of Cu(II)DMAP complexes

Infrared spectra were recorded for the solid products on a PE 580 spectrophotometer supplied with a data station. Ligand-field spectra in the solid state were recorded on a Perkin Elmer instrument (type 330), using the diffuse reflectance method and MgO as a reference.

Solution ligand-field spectra were recorded on a Cary 14 instrument and UV spectra on a PYE Unicam SP 8-200 UV/Vis spectrophotometer at 298.2 K. EPR spectra of the frozen solutions and of the powdered compounds were recorded on a Varian E4 spectrometer (77 K and 300 K).

Copper analyses were performed by complexometric titrations with EDTA using standard procedures. Chlorine was determined by standard methods, whereas C, H and N were determined by commercial laboratories.

Results

Catalytic experiments

Verlaan *et al.* [1] have reported that for copper complexes of DMAP the reoxidation of Cu(I) to Cu(II) is rate determining. They only used Cl^- counter-ions for copper and always added KOH ($[\text{OH}^-]_0 = [\text{Cu}^{2+}]$). In the present study the following counter-ions were considered: Cl^- , NO_3^- and BF_4^- . Cl^- ions may act as bridging ions in dinuclear copper complexes [8, 9], whereas NO_3^- and BF_4^- ions cannot do so since they are weakly- and non-coordinating counter-ions for copper, respectively.

It was first established by performing O_2 pressure-dependent experiments that, for all complexes used in this study, the reoxidation of Cu(II) is rate determining for the standard pressure of 101.3 kPa and other standard conditions (see Experimental). The catalytic activity was measured as a function of DMAP/Cu in the absence of initial hydroxide ions for Cl^- , NO_3^- and BF_4^- counter-ions. The results are depicted in Fig. 1 (three lower curves). It is obvious that these coordination complexes are catalytically active even without initial OH^- addition. In Fig. 1 one can also see that for the weakly and non-coordinating copper counter-ions the plot of R vs. DMAP/Cu levels off for DMAP/Cu values exceeding 4. As preliminary spectroscopic studies indicated the existence of species with the composition $[\text{Cu}^{2+}(\text{DMAP})_4(\text{BF}_4^-)_2]$ as predominant, it seemed most appropriate to carry out most of the catalytic experiments with DMAP/Cu = 4.

From earlier investigations it is known that the activity of copper amine complexes can be significantly enhanced by the addition of hydroxide

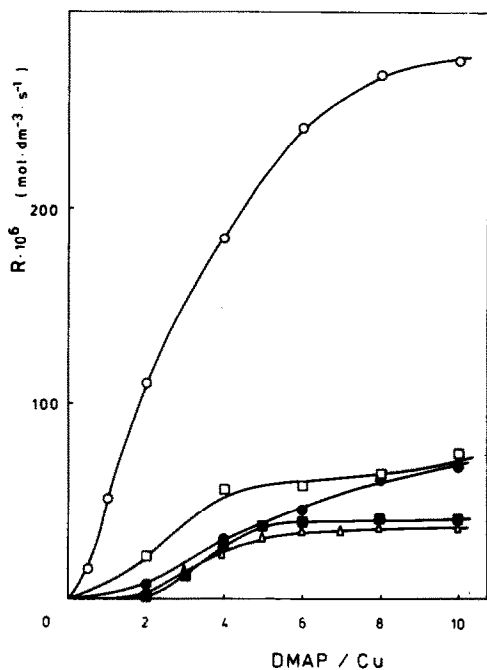


Fig. 1. Dioxygen consumption rate R as a function of DMAP/Cu. Standard conditions (see experimental). $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0$ for $\circ = 1:n:2:0:0:1$; for $\square = 1:n:0:2:0:1$; for $\bullet = 1:n:2:0:0:0$; for $\blacksquare = 1:n:0:2:0:0$; for $\triangle = 1:n:0:0:2:0$.

[6, 8, 11]. This was also verified for our DMAP-based catalysts. For Cl^{-} counter-ions, LiOH or KOH was added. In the case of NO_3^{-} (and also BF_4^{-}) the addition of these hydroxides resulted in the precipitation of LiNO_3 (or LiBF_4) and KNO_3 (or KBF_4). However, no precipitates were formed with $(\text{CH}_3)_4\text{N}(\text{OH})$, and in the case of NO_3^{-} this hydroxide was used. Experiments with Cl^{-} counter-ions made clear that the reaction rate is independent of the counter-cation of the hydroxide. For both coordinating and weakly coordinating counter-ions, optimum activity was found at $\text{OH}/\text{Cu} = 1$ (see Fig. 2). In Fig. 2 it is also demonstrated that the optimum OH/Cu value of 1 can also be obtained for $\text{DMAP}/\text{Cu} = 2$. Furthermore, the presence of coordinating counter-ions (Cl^{-}) seems to be of great importance for the accelerating effect of hydroxide addition.

Once the optimum OH/Cu ratio had been determined, the dioxygen consumption rate was measured as a function of DMAP/Cu with $(\text{OH}/\text{Cu})_0 = 1$ for both Cl^{-} and NO_3^{-} counter-ions. The results are also depicted in Fig. 1 (two upper curves) together with the hydroxide-free experiments, to allow easy comparison. The increase in activity by addition of OH^{-} is striking, especially for Cl^{-} . It should be noted that for reaction rates exceeding $200 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$, the dioxygen diffusion from the gas phase to the reaction medium becomes rate determining. For this reason the curve for the system $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{OH}^{-} = 1:n:2:1$ levels off for $n \geq 6$.

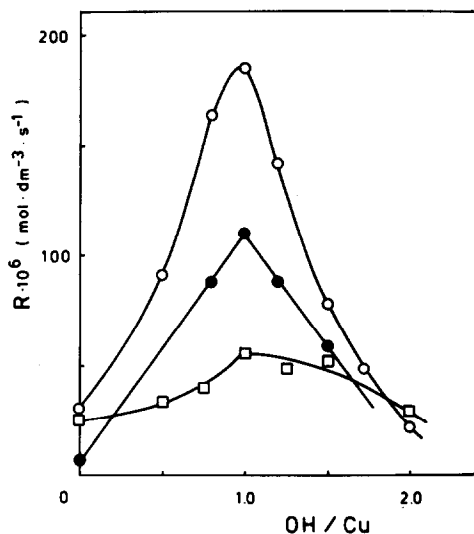


Fig. 2. Dioxygen consumption rate R as a function of OH/Cu . Standard conditions (see experimental). $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0$ for $\circ = 1:4:2:0:0:n$; for $\bullet = 1:2:2:0:0:n$; for $\square = 1:4:0:2:0:n$.

In Fig. 3 the dioxygen consumption rate R is given as a function of Cl/Cu , both in the absence of hydroxide and in the presence of initially added $(\text{CH}_3)_4\text{N}(\text{OH})$ with $(\text{OH}/\text{Cu})_0 = 1$. Copper ions were added as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ salt. Cl/Cu was varied by addition of methanolic solutions

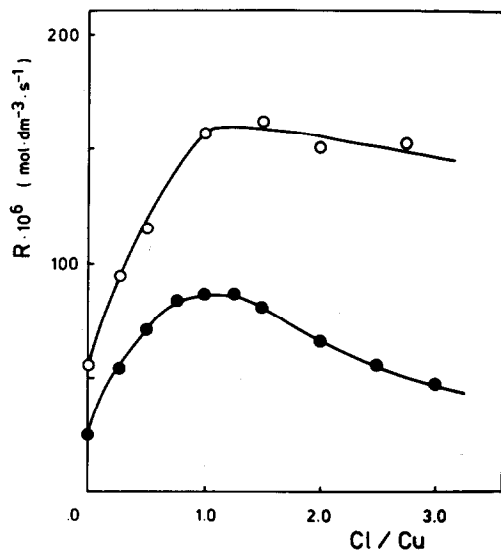


Fig. 3. Dioxygen consumption rate R as a function of Cl/Cu . Standard conditions (see experimental). $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0$ for $\circ = 1:4:n:2:0:1$; for $\bullet = 1:4:n:2:0:0$.

of tetramethylammonium chloride of a known concentration. It is clear that substitution of the coordinating Cl^- ions for the weakly-coordinating NO_3^- ions enhances the catalytic activity of the complex with a broad optimum around $\text{Cl}/\text{Cu} = 1$. From the dioxygen consumption curves, it could be derived that the Cl^- complexes remain more active over the whole conversion range of the reaction. From comparison of Figs. 2 and 3, it can be concluded that starting with $(\text{OH}/\text{Cu})_0 = 1$ the dioxygen consumption rate can be enhanced by Cl^- addition up to $\text{Cl}/\text{Cu} = 1$ and not by further OH^- addition. On the other hand, when $\text{Cl}/\text{Cu} = 1$, R can be enhanced by OH^- addition up to $\text{OH}/\text{Cu} = 1$ and not by further Cl^- addition.

Finally, the reaction rate of the oxidative coupling was determined as a function of $[\text{DMP}]$ in the range of $0.02 - 0.08 \text{ mol dm}^{-3}$. Figure 4 shows that all reaction rates increase nearly linearly with $[\text{DMP}]$, even in cases where the reoxidation of $\text{Cu}(\text{I})$ is rate determining, *i.e.* for $[\text{DMP}] \geq 0.04 \text{ mol dm}^{-3}$.

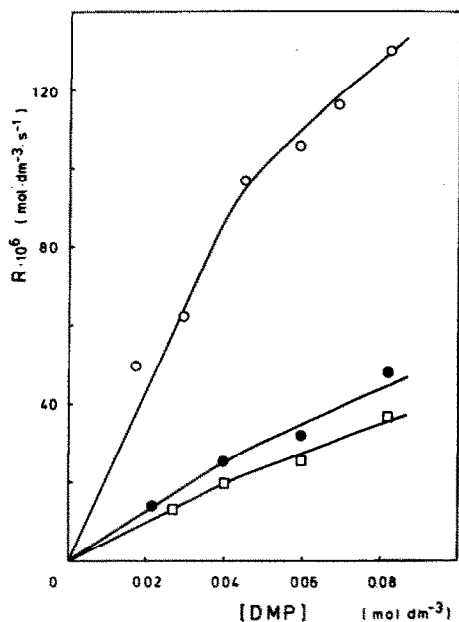


Fig. 4. Dioxygen consumption rate R as a function of $[\text{DMP}]$. Standard conditions, except $[\text{DMP}]$ (see experimental). $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{NO}_3^-:\text{BF}_4^-:(\text{OH}^-)_0$ for $\circ = 1:2:2:0:0:1$; for $\bullet = 1:4:2:0:0:0$; for $\square = 1:4:0:2:0:0$.

The initiation period Δt of the oxidative coupling reaction

The oxidative coupling reaction does not always start as soon as DMP is added to the catalyst solution. This phenomenon was investigated. Δt is defined as the time interval between the addition of the substrate DMP and the start of the dioxygen consumption. Irrespective of the nature of the copper counter-ion, Δt decreases when DMAP/Cu is enhanced. For BF_4^-

TABLE 1

Initiation period Δt as a function of the composition of the catalyst solution; standard conditions (see experimental)

System $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{NO}_3^-:\text{BF}_4^-:(\text{OH}^-)_0$	Δt (s)	System $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{NO}_3^-:\text{BF}_4^-:(\text{OH}^-)_0$	Δt (s)
1 : 2 : 0 : 2 : 0 : 0	1800	1 : 4 : 0 : 2 : 0 : 0	50
1 : 2 : 0 : 0 : 2 : 0	1100	1 : 4 : 0 : 2 : 0 : 1	27
1 : 2 : 2 : 0 : 0 : 0	84	1 : 4 : 0 : 2 : 0 : 2	54
1 : 2 : 0 : 2 : 0 : 0	1800	1 : 4 : 2 : 0 : 0 : 0	12
1 : 4 : 0 : 2 : 0 : 0	50	1 : 4 : 2 : 0 : 0 : 1	2
1 : 10 : 0 : 2 : 0 : 0	39	1 : 4 : 2 : 0 : 0 : 2	36
1 : 2 : 2 : 0 : 0 : 0	84	1 : 2 : 2 : 0 : 0 : 1	5
1 : 4 : 2 : 0 : 0 : 0	12	1 : 4 : 2 : 0 : 0 : 1	2
1 : 10 : 2 : 0 : 0 : 0	9	1 : 10 : 2 : 0 : 0 : 1	0
1 : 4 : 0 : 2 : 0 : 0	50	1 : 4 : 2 : 0 : 0 : 1	27
1 : 4 : 1 : 2 : 0 : 0	21	1 : 4 : 1 : 2 : 0 : 1	1
1 : 4 : 2 : 2 : 0 : 0	24	1 : 4 : 2.75 : 2 : 0 : 1	13

and NO_3^- counter-ions, Δt values are comparable and, especially when DMAP/Cu is low, much higher than those for Cl^- (see Table 1). For all counter-ions Δt is reduced by addition of hydroxide, and minima around $(\text{OH}/\text{Cu})_0 \cong 1$ are obtained. Addition of more OH^- leads to higher values of Δt . However, for the system with $\text{Cu}^{2+}:\text{DMAP}:\text{NO}_3^-:\text{OH}^- = 1:4:2:1$, Δt can be reduced by Cl^- addition. Addition of Cl^- ions to the system with $\text{Cu}^{2+}:\text{DMAP}:\text{NO}_3^- = 1:4:2$ leads to a decrease of Δt up to a ratio of $\text{Cl}/\text{Cu} \cong 1$. A further decrease of Δt is possible by addition of hydroxide (up to $(\text{OH}/\text{Cu})_0 \cong 1$, see above) or extra DMAP. The lowest values of Δt are obtained for systems with Cl^- counter-ions and $(\text{OH}/\text{Cu})_0 = 1$. Enhancement of DMAP/Cu only slightly reduces Δt in that case. Some interesting data are listed in Table 1.

Specificity of the catalysts and intrinsic viscosity, $[\eta]$, of the produced PPO

By means of UV spectroscopy the conversion of DMP to DPQ was determined for the different systems. A distinction was made between systems with strongly coordinating counter-ions and systems with weakly coordinating counter-ions, Cl^- and NO_3^- respectively. Moreover, the influence of DMAP/Cu on specificity was investigated. Finally, the influence of initially added hydroxide was studied for the systems with Cl^- counter-ions. The results are summarized in Table 2. It is obvious that the production of the undesired byproduct DPQ can be suppressed to a great extent when strongly coordinating counter-ions (Cl^-) are used instead of weakly coordinating counter-ions (NO_3^-). PPO production is also favoured when the DMAP/Cu ratio is increased. This effect is generally attributed to an en-

TABLE 2

PPO production out of DMP as a function of the nature of the counter ion, DMAP/Cu and $(\text{OH}/\text{Cu})_0$; standard conditions were used

System							% DMP transformed into PPO
$\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{NO}_3^-:\text{BF}_4^-:(\text{OH}^-)_0$							
1 : 2 : 0 : 2 : 0 : 0							62
1 : 2 : 2 : 0 : 0 : 0							80
1 : 2 : 2 : 0 : 0 : 1							91
1 : 4 : 0 : 2 : 0 : 0							90
1 : 4 : 2 : 0 : 0 : 0							94
1 : 4 : 2 : 0 : 0 : 1							95
1 : 4 : 2 : 0 : 0 : 2							96
1 : 8 : 0 : 2 : 0 : 0							96
1 : 8 : 2 : 0 : 0 : 0							96
1 : 8 : 2 : 0 : 0 : 1							96
1 : 4 : 0 : 2 : 0 : 1							94
1 : 4 : 0 : 2 : 0 : 2							96
1 : 4 : 1 ^a : 2 : 0 : 1							94
1 : 4 : 2 ^a : 2 : 0 : 1							94

^aAdded as $(\text{CH}_3)_4\text{NCl}$.

hancement in basicity [4]. On addition of hydroxide ions the DPQ production for DMAP/Cu = 4 can be limited to about 5%, irrespective of the nature of the counter-ions. This specificity is also reached without initial OH⁻ addition when relatively high DMAP/Cu values are used.

For the system Cu²⁺:DMAP:Cl⁻:OH⁻ = 1:4:2:1 with standard conditions but extra high [DMP] = 0.27 mol dm⁻³, the reaction product was isolated and characterized. The PPO was obtained as a white powder with an intrinsic viscosity, $[\eta]$, of 44.3 ml g⁻¹. This corresponds to $\bar{M}_v = 4.3 \times 10^4$ using the Mark-Houwink relation with $K = 4.83 \times 10^{-2}$ ml g⁻¹ and $\alpha = 0.64$ in chloroform at 298.2 ± 0.1 K [12].

Structure of the complexes in solution

In order to explain the results of the catalytic experiments, the structure of the active complexes in solution was investigated by ligand-field and EPR spectroscopy. The results are given below.

UV-Visible spectroscopy

Usually transition metal complexes exhibit two types of UV/Vis absorptions apart from ligand and counter-ion spectra [13]:

(i) The d-d absorption caused by excitation of an electron from a d-orbital to another d-orbital.

(ii) Charge-transfer spectra involving electronic transitions between the metal and the ligands.

Usually the d-d transitions are located in the visible and near IR region, and the charge transfer transitions in the near UV region. Although one should be careful when deriving quantitative data, the spectra may give an indication of the composition of the complex. For this purpose, UV spectra were recorded of solutions of complexes with varying ligand-to-copper ratios. Furthermore, the type of counter-ion was varied. Standard conditions were used without DMP addition, and no hydroxide was initially added unless otherwise stated.

In Fig. 5 the d-d absorption spectra of the Cu(II) DMAP complexes with Cl⁻ counter-ions are drawn for DMAP/Cu values varying from 0.5 to 13. The spectrum of CuCl₂ without added DMAP in the reaction mixture is also present. The double maximum around 800 nm should be noted. Figure 5 shows an ill-defined isosbestic point for all DMAP/Cu values ≥ 2 . The appearance of an isosbestic point suggests a change from one coloured species into another one [14], although the lack of clarity of the point indicates that another process might be occurring in addition.

In Fig. 6, the charge-transfer absorbance (A_{CT}) at 366 nm of the Cu(II)-DMAP complexes with Cl⁻ counter-ions is given as a function of DMAP/Cu. The curve shows a sharp bend at DMAP/Cu = 2, suggesting the formation of another type of compound.

In Fig. 7 the d-d-absorption spectra of the Cu(II)DMAP complexes with BF₄⁻ counter-ions are given for DMAP/Cu values within the range 0.5 to 10. The difference between these spectra for non-coordinating

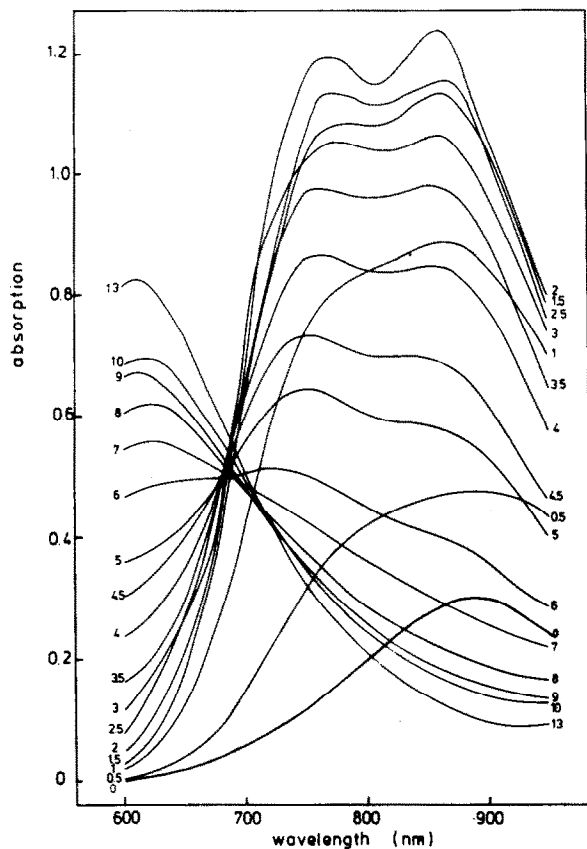


Fig. 5. d-d absorption spectra for various DMAP/Cu values for the system with Cu^{2+} : DMAP: Cl^- : NO_3^- : BF_4^- : $(\text{OH}^-)_0 = 1:n:2:0:0:0$ in the standard reaction mixture (without DMP) with standard complex concentrations (see experimental). DMAP/Cu values are indicated in the Figure.

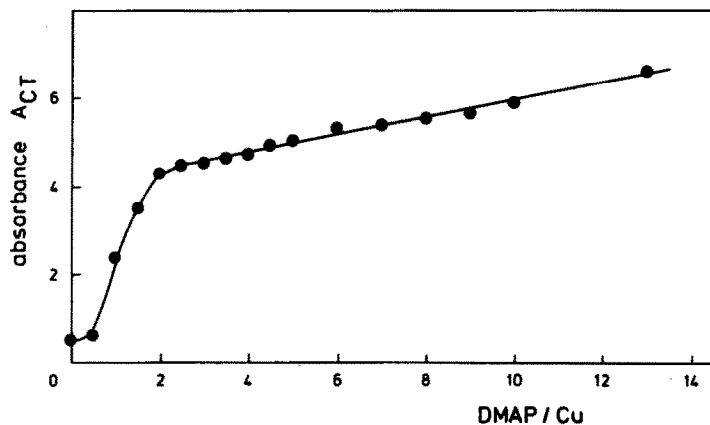


Fig. 6. Charge-transfer absorbance (A_{CT}) at 366 nm as a function of DMAP/Cu for the system with Cu^{2+} : DMAP: Cl^- : NO_3^- : BF_4^- : $(\text{OH}^-)_0 = 1:n:2:0:0:0$. Standard conditions (see experimental), no DMP.

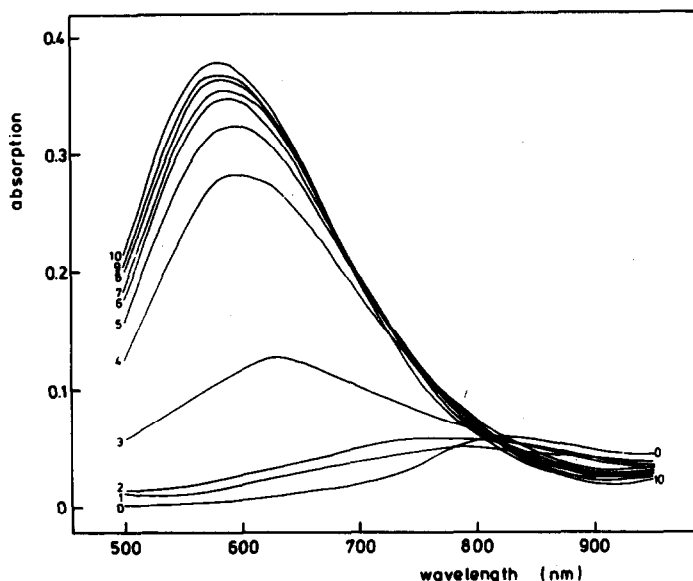


Fig. 7. d-d absorption spectra for various DMAP/Cu values for the system with Cu^{2+} : DMAP: Cl^- : NO_3^- : BF_4^- : $(\text{OH}^-)_0 = 1:n:0:0:2:0$ in the standard reaction mixture (no DMP) with standard complex-concentrations (see experimental). DMAP/Cu values are indicated in the Figure.

counter-ions and the spectra drawn in Fig. 5 for coordinating counter-ions is obvious.

In Figs. 5 and 7 the maxima at $\lambda = 615$ and $\lambda = 579$ nm, respectively, correspond to the absorptions of mononuclear species with the general formula $\text{Cu}(\text{DMAP})_n\text{X}_2$ with $\text{X} = \text{Cl}^-$ and BF_4^- , respectively, and $n \geq 4$. In Fig. 8 the absorbances of both mononuclear complexes are given as a function of DMAP/Cu. The difference is striking and should be compared with the curves of R vs. DMAP/Cu for the corresponding complexes (see Fig. 1).

So far, no OH^- ions had been initially added to the complex solutions for UV spectroscopy. Now the results of experiments carried out with $(\text{OH}/\text{Cu})_0 = 1$ will be presented. In Fig. 9, the d-d absorption spectra of the complexes with Cl^- are given for different ligand-to-copper ratios ($0.5 \leq \text{DMAP}/\text{Cu} \leq 10$). The absorption maxima at 620 nm are again attributed to the absorption of mononuclear species. For small DMAP/Cu values, these species are hardly present, and in fact double maxima are found around 800 nm. Figure 9 shows an ill-defined isosbestic point for $\text{DMAP}/\text{Cu} \geq 1$.

In Fig. 10 the absorbance of the mononuclear complex, as derived from Fig. 9, is given as a function of DMAP/Cu. It is clear that on addition of hydroxide to the $\text{Cu}(\text{II})\text{DMAP}$ complexes with Cl^- counter-ions, the absorption of mononuclear complex as a function of DMAP/Cu is significantly changed (compare Fig. 8).

For complexes with BF_4^- counter ions some UV experiments were carried out with hydroxide addition. The absorbance of the mononuclear

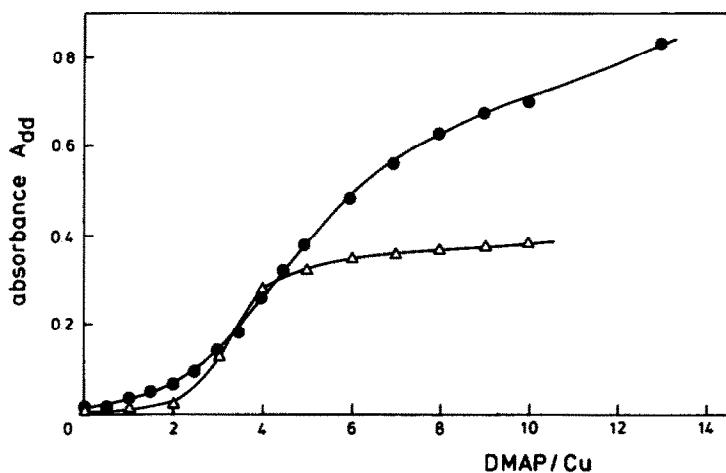


Fig. 8. Absorbance of mononuclear complexes as a function of DMAP/Cu for the system with $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0 = 1:n:2:0:0:0$ as derived from Fig. 5 (●; $\lambda_{\text{max, mono}} = 615 \text{ nm}$) and for the system with $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0 = 1:n:0:0:2:0$ as derived from Fig. 7 (Δ; $\lambda_{\text{max, mono}} = 579 \text{ nm}$). Standard conditions (see experimental), no DMP.

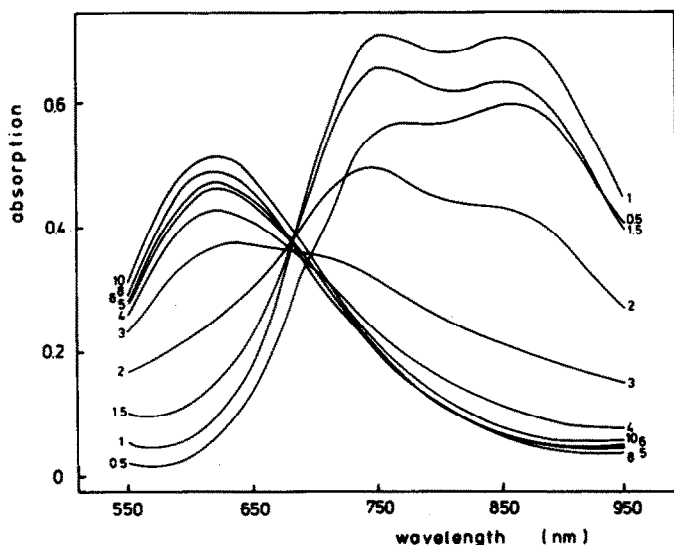


Fig. 9. d-d absorption spectra for various DMAP/Cu values for the system with $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0 = 1:n:2:0:0:1$. Standard conditions without DMP (see experimental). DMAP/Cu values are indicated in the Figure.

complex was determined for DMAP/Cu values of 2, 4 and 6 ($\lambda_{\text{max}} = 576 \text{ nm}$). The spectra of all three systems show a single d-d absorption maximum. The absorbance at 576 nm is plotted in Fig. 10, yielding a curve similar to that for Cl^{-} counter-ions.

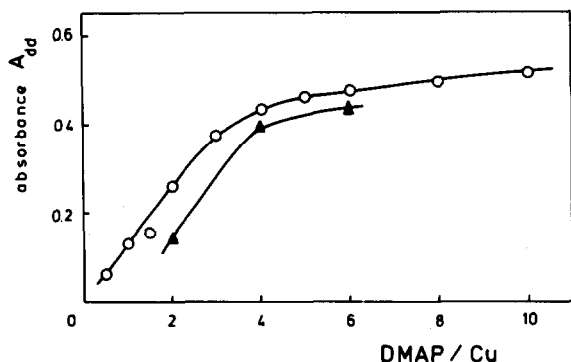


Fig. 10. Absorbance of mononuclear complexes as a function of DMAP/Cu for the system with $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0 = 1:n:2:0:0:1$ as derived from Fig. 9 (O; $\lambda_{\text{max,mono}} = 620 \text{ nm}$) and for the system with $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^{-}:\text{NO}_3^{-}:\text{BF}_4^{-}:(\text{OH}^{-})_0 = 1:n:0:0:2:1$ (▲; $\lambda_{\text{max,mono}} = 576 \text{ nm}$).

EPR and ligand field spectroscopy on solid and dissolved Cu(II)DMAP complexes

In an exploratory investigation using CuCl_2 , $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{BF}_4)_2$ (all hydrated) and methanol or $\text{MeOH}/1,2$ -dichlorobenzene as solvents, the following solids have been isolated and characterized by chemical analyses [15]: $\text{CuCl}_2(\text{DMAP})_2$ (green), $\text{Cu}_4\text{OCl}_6(\text{DMAP})_4$ (orange-brown), $\text{CuCl}_2(\text{DMAP})_4(1,2\text{-dichlorobenzene})_2(\text{H}_2\text{O})_2$ (grayish-black), $\text{CuCl}_2(\text{DMAP})_4(\text{H}_2\text{O})_2$ (blue), $\text{Cu}(\text{DMAP})_4(\text{NO}_3)_2$ and $\text{Cu}(\text{DMAP})_4(\text{BF}_4)_2$.

The solid state structure of the last compound has been determined in detail with the aid of X-ray analysis (*vide infra*). The other compounds having 4 DMAP ligands per Cu(II) are believed to have the same basic structure, *i.e.* a tetragonal coordination geometry for the $\text{Cu}(\text{DMAP})_4^{2+}$ unit, with two additional ligands in the apical coordination positions 5 and 6. The spectral properties of all these solid compounds are the same, in having a ligand-field band maximum at about $17\,000 \text{ cm}^{-1}$ and EPR powder parameters of $g_{\parallel} = 2.24 \pm 0.01$, $A_{\parallel} = 180 \pm 2 \text{ Gauss}$ and $g_{\perp} = 2.04 \pm 0.01$, all typical for a species CuN_4 [16]. The grayish-black compound $\text{CuCl}_2(\text{DMAP})_4(1,2\text{-dichlorobenzene})_2(\text{H}_2\text{O})_2$ apparently contains lattice molecules of 1,2-dichlorobenzene, the stacking of which with DMAP is probably responsible for the black color (bands at $26\,300$ and $29\,900 \text{ cm}^{-1}$). The compound Cu_4OCl_6 most likely is an analogue of the well-known series $\text{Cu}_4\text{OCl}_6(\text{Rpy})_4$ [17].

In order to determine whether we are dealing with mononuclear or dinuclear Cu(II)DMAP complexes in solution, UV experiments are insufficient and EPR experiments should be performed. Mononuclear copper complexes exhibit an EPR signal because of the presence of an unpaired electron in the copper d-orbitals. Interaction of this unpaired electron with the magnetic moments of the copper nucleus and the nuclei of the ligands may result in hyperfine structures. Dinuclear copper complexes are often

EPR-silent [18], or show typical $S = 1$ spectra. EPR spectra were recorded in frozen MeOH/1,2-dichlorobenzene solutions at 77 K. The different systems of investigation are listed in Table 3.

The influence of an altering complex composition on the relative EPR-intensity is also given. Standard conditions were used and no DMP was added. Please note that Table 3 gives no more than some general trends with respect to the relation between complex composition and EPR intensity. No attempts were undertaken to integrate the EPR signals. Nevertheless, it is obvious that the EPR intensity, in other words the concentration of mononuclear Cu(II)DMAP complex, generally increases when DMAP/Cu is enhanced. On the other hand, addition of copper-coordinating counterions (Cl^- and/or OH^-) results in reduced EPR intensity.

Concerning the EPR spectra, it should be noted that nearly all systems show the presence of one major species with the EPR parameters $g_{\parallel} = 2.24 \pm 0.01$, $A_{\parallel} = 180 \pm 2$ Gauss and $g_{\perp} = 2.04 \pm 0.01$. In most cases, even nitrogen superhyperfine splitting is found with values of $A_{N\parallel} = 14$ Gauss and $A_{N\perp} = 14$ Gauss. All these values are without any doubt typical for a species CuN_4 [16]. These parameters are found even when $(\text{OH}/\text{Cu})_0 = 1$ (although the intensity is much weaker in those cases). An example of an EPR spectrum with nitrogen superhyperfine splitting is shown in Fig. 11a. The only investigated systems that do not show the presence of a species with the mentioned

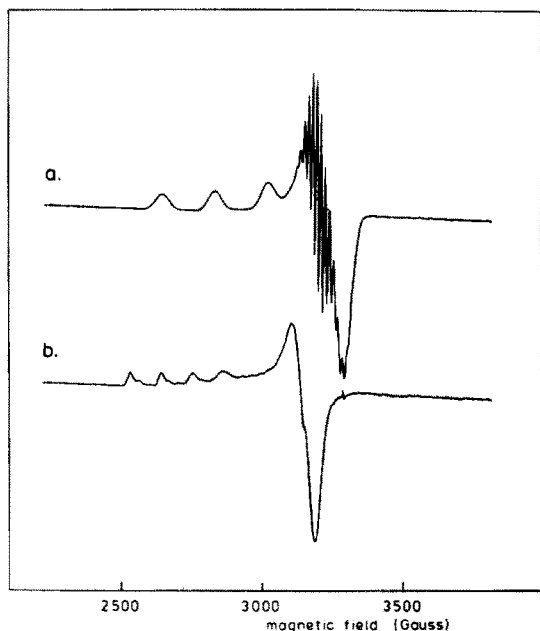


Fig. 11. EPR spectra of two representative systems in MeOH/1,2-dichlorobenzene (2/13 vol.%) at 77 K. (a) $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{NO}_3^-:\text{BF}_4^-:(\text{OH}^-)_0 = 1:4:2:0:0:0$; note the superhyperfine structure. (b) $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{NO}_3^-:\text{BF}_4^-:(\text{OH}^-)_0 = 1:1:2:0:0:0$; no superhyperfine structure is visible.

TABLE 3

Relative EPR intensities of frozen solutions of Cu(II)DMAP complexes with various compositions; standard conditions for [Cu(II)] and solvent compositions; $T = 77$ K

Series	System Cu ²⁺ : DMAP : Cl ⁻ : NO ₃ ⁻ : BF ₄ ⁻ : (OH ⁻) ₀	<i>n</i> values	Remarks on EPR intensity
I	1 : <i>n</i> : 2 : 0 : 0 : 0 : 0	1, 2, 4 or 6	continuous increase with increasing <i>n</i>
II	1 : <i>n</i> : 2 : 0 : 0 : 1	1/2, 1, 4, 6 or 8	decrease with respect to series I; increase with increasing <i>n</i>
III	1 : <i>n</i> : 0 : 2 : 0 : 0	2, 4 or 6	increase from <i>n</i> = 2 to 4; leveling off from <i>n</i> = 4 to 6
IV	1 : 4 : <i>n</i> : 2 : 0 : 0	2 or 4	slight decrease with respect to series III
V	1 : <i>n</i> : 0 : 0 : 2 : 0	1, 4, 6 or 8	strong increase up to <i>n</i> = 4; slight increase from <i>n</i> = 4 to <i>n</i> = 8
VI	1 : 4 : 0 : 0 : 2 : <i>n</i>	0, 1/8, 1/4, 1/2, 1 or 2	decrease with increasing <i>n</i>

EPR parameters are the following: $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^- = 1:1:2$ (see Fig. 11b) and $\text{Cu}^{2+}:\text{DMAP}:\text{BF}_4^- = 1:1:2$, where an EPR signal is present but no nitrogen superhyperfine splitting is found and $A_{\parallel} = 108$ Gauss; $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{OH}^- = 1:0.5:2:1$ and $\text{Cu}^{2+}:\text{DMAP}:\text{BF}_4^-:\text{OH}^- = 1:4:2:2$, where the EPR intensity is practically zero and no mononuclear complexes seem to be present.

Apart from some exceptions, our observations suggest that the only detectable EPR species is the $\text{Cu}(\text{DMAP})_4^{2+}$ ion (with varying apical ligands having only very small effects), and that other species are EPR-silent and most probably dimeric (or of a higher order of association). Therefore, the ligand-field spectra were recorded in the presence and absence of excess OH^- and Cl^- . These spectra unambiguously showed that the only species that is present when $\text{DMAP}/\text{Cu} = 4$ (for BF_4^-) or larger (for NO_3^-) or much larger (for Cl^-) is the species CuN_4 , provided that no OH^- is added.

Thus, in summary, we believe that in nearly all cases the species $\text{Cu}(\text{DMAP})_4\text{X}_2$ is present. This species changes into EPR-silent (probably dimeric) species upon gradual addition of Cl^- and/or OH^- .

Description of the X-ray structure of $\text{Cu}(\text{DMAP})_4(\text{BF}_4)_2$

As mentioned above, spectroscopic studies indicated the existence of the mononuclear species $\text{Cu}(\text{DMAP})_4(\text{BF}_4)_2$ in the reaction medium. Furthermore, this species showed significant activity in our reaction rate studies, even without added OH^- . Therefore it was decided to study the X-ray structure to see whether or not unusual features are present in the coordination sphere. The details of the structure will be published elsewhere [15]. Only a brief description will be given here, which is needed to understand the spectroscopic and catalytic properties. $\text{Cu}(\text{DMAP})_4(\text{BF}_4)_2$ crystallizes in the triclinic space group P_1 , with $a = 10.970$, $b = 16.685$, $c = 20.315$ Å,

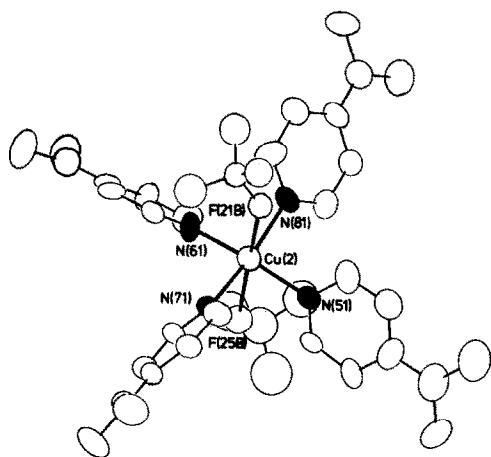


Fig. 12. ORTEP drawing of one of the two molecular units in $\text{Cu}(\text{DMAP})_4(\text{BF}_4)_2$. Relevant distances are: (in Å) $\text{Cu}-\text{N}51 = 2.01$; $\text{Cu}-\text{N}61 = 1.99$; $\text{Cu}-\text{N}71 = 2.03$; $\text{Cu}-\text{N}81 = 2.02$; $\text{Cu}-\text{F}21 = 2.75$; $\text{Cu}-\text{F}25 = 2.66$.

and the angles $\alpha = 76.713^\circ$, $\beta = 73.289^\circ$, $\gamma = 78.094^\circ$, $Z = 4$; calculated density 1.41 g cm^{-3} (measured 1.40). The copper(II) is coordinated by four DMAP ligands through the pyridine nitrogen, in a tetragonal geometry; two weakly bound F-atoms of (disordered) BF_4 groups complete the coordination. The long Cu—F distances are considered to be semi-coordinating. The unit cell contains two crystallographically independent Cu(II) ions, having about the same coordination distances and angles. Figure 12 presents the structure of one formula unit. Some relevant distances are given in the Figure caption. The Cu—F semi-coordinating distances vary for the several (disordered) sites (2.55 - 2.90 Å). It is highly likely that these BF_4 anions will dissociate from the Cu(II) ion in solution.

Discussion

It is our goal to explain the catalytic results using the determined structure of the active Cu(II)DMAP complexes in solution. Therefore the results of the spectroscopic studies will be discussed first.

Structure of Cu(II)DMAP complexes

Without addition of hydroxide

Figure 5 shows that for copper-coordinating Cl^- counter-ions, in the absence of OH^- , the d-d absorption curves exhibit an isosbestic point for $\text{DMAP/Cu} \geq 2$, although the lack of clarity of the point indicates that another process might also be occurring.

The presence of this isosbestic point indicates that one coloured species in solution is transformed into another upon changing the DMAP/Cu ratio. This is in agreement with Fig. 6. The charge-transfer absorbance at 366 nm shows a sharp bend at $\text{DMAP/Cu} = 2$. Returning to Fig. 5, we see that for $\text{DMAP/Cu} < 6$ a double d-d absorption maximum, with maximum absorbance at $\text{DMAP/Cu} = 2$, is present, which changes into a single maximum at shorter wavelength for higher DMAP/Cu values. The appearance of double maxima at about 800 - 900 nm does not agree with a square-planar coordination of Cu(II). Usually, five-coordinated Cu(II) compounds yield maxima in this area [13]. The single maximum at about 615 nm is attributed to the absorption of mononuclear complexes. (However, dinuclear species $[(\text{DMAP})_2\text{Cu}(\text{OH})_2\text{Cu}(\text{DMAP})_2]^{2+}$ cannot be excluded completely [19].) In other words, we believe that for Cl^- counter-ions only dinuclear Cu(II)-DMAP complexes are formed for $\text{DMAP/Cu} < 2$. In Fig. 6 this is shown as a strong increase of A_{CT} with increasing DMAP/Cu ratio, and in Fig. 5 as an increasing absorbance around 800 nm. For $\text{DMAP/Cu} > 2$ these dinuclear complexes are transformed into mononuclear complexes. This transformation results in a smaller increase of A_{CT} with increasing DMAP/Cu for $\text{DMAP} > 2$ and in a collapse of the absorbance around 800 nm in Fig. 5. The increasing concentration of the mononuclear complex is shown in Fig. 8, indicating that the transformation is still incomplete even for $\text{DMAP/Cu} =$

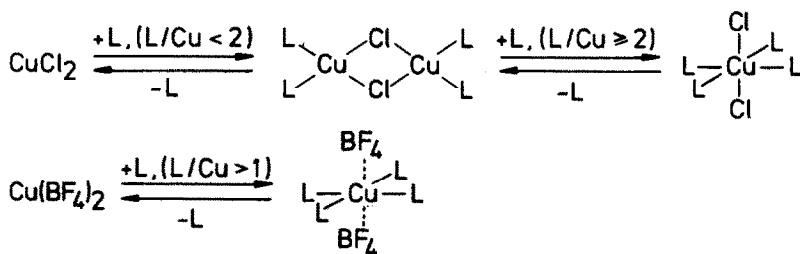
13. From this we conclude that the copper complexes of DMAP with Cl^- as coordinating non-apical ions are relatively strong.

Our ideas mentioned above are in complete agreement with the results of the EPR experiments (see Table 3). For the system $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^- = 1:n:2$, the EPR intensity increases with n . In other words, the concentration of the only present EPR-active species $\text{Cu}(\text{DMAP})_4\text{Cl}_2$ is enhanced. For $n = 1$, no nitrogen superhyperfine splitting is resolved in the EPR spectrum, suggesting that any DMAP is coordinated to EPR-silent $\text{Cu}(\text{II})$. The observed EPR signal at $n = 1$ relates to free CuCl_2 ($A_{\parallel} = 108$ Gauss), and all $\text{Cu}(\text{II})\text{DMAP}$ complexes are di- or polynuclear.

Figure 7 shows that, for non-coordinating BF_4^- counter-ions in the absence of OH^- , no d-d absorptions typical for dinuclear copper complexes (around 800 nm) are present. The curves exhibit only single maxima, in agreement with a CuN_4 chromophore ($\lambda_{\text{max}} = 579$ nm).

In Fig. 8 the absorbance at 579 nm is given as a function of DMAP/Cu . It is obvious that the formation of mononuclear $\text{Cu}(\text{II})\text{DMAP}$ complexes is nearly complete at $\text{DMAP}/\text{Cu} \cong 4$. Again, this agrees with our EPR results (Table 3). For the system $\text{Cu}^{2+}:\text{DMAP}:\text{BF}_4^- = 1:n:2$ the EPR intensity only slightly increases on going from $n = 4$ to $n = 8$. In the case of $n = 1$, again, no nitrogen superhyperfine splitting is found (and the catalytic activity is practically zero, see Fig. 1). The above considerations are presented schematically in Scheme 4, where L represents a DMAP unit.

No OH^- addition:



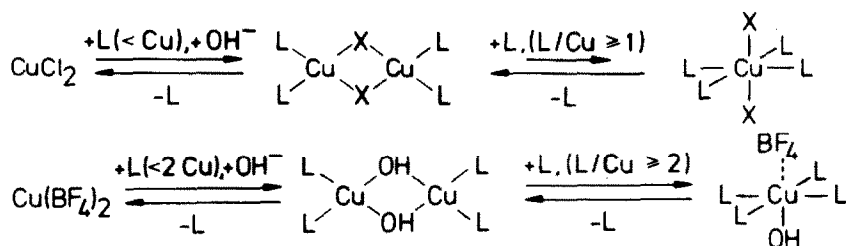
Scheme 4.

With addition of hydroxide

Figure 9 shows the d-d absorption curves for the system $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{OH}^- = 1:n:2:1$. The double maxima around 800 nm for $n \leq 2$ and the single maxima at 620 nm for higher DMAP/Cu values, together with the presence of an isosbestic point for $n \geq 1$, again point to a transformation of dinuclear copper complexes into mononuclear complexes, although the lack of clarity of the isosbestic point again might indicate that in addition another process is occurring. In this case, maximum absorbance around 800 nm is achieved at $\text{DMAP}/\text{Cu} = 1$. The distortion of the square-planar coordination of $\text{Cu}(\text{II})$ (*vide supra*) is observed only for $\text{DMAP}/\text{Cu} < 3$, whereas for $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^- = 1:n:2$ this was found for n -values up to 6.

The transformation of dinuclear into mononuclear complexes for DMAP/Cu > 4 seems to be hindered in the case of initially added OH⁻. In this respect, one should compare the upper curve in Fig. 10, where $A_{\text{dd,mono}}$ at $\lambda = 620$ nm is given as a function of DMAP/Cu, with the upper curve in Fig. 8. The increase of $A_{\text{dd,mono}}$ with increasing DMAP/Cu agrees with our EPR results. For BF₄⁻ counter-ions with (OH/Cu)₀ = 1, the double maxima around $\lambda = 800$ nm have already vanished at DMAP/Cu = 2, indicating that few dinuclear Cu(II) complexes still exist. As OH⁻ ions may act as strongly bridging ions [6, 8, 11] a dihydroxo-bridged dinuclear copper(II) complex is assumed for BF₄⁻ counter-ions at DMAP/Cu < 2. As above, a Scheme of the proposed transformations is presented for the sake of clarity.

OH⁻ addition (OH/Cu=1, X=Cl⁻ or OH⁻):



Scheme 5.

In summary, the following conclusions can be drawn concerning the structure of the catalytically active complexes in all systems investigated. The only mononuclear complexes present in relatively large amounts (EPR, ligand field) are of the type Cu(DMAP)₄²⁺X₂⁻ (where X = BF₄, NO₃, Cl and/or OH). In presence of coordinating counter-ions (Cl, OH) both mononuclear and dinuclear complexes are simultaneously present, the mono/di ratio being dependent on DMAP/Cu. For non-coordinating copper counter-ions, only mononuclear complexes occur in the absence of OH⁻. In all systems the concentration of the species Cu(DMAP)₄²⁺ can be reduced by addition of coordinating counter-ions, and enhanced by an increase of the DMAP/Cu ratio.

Finally, the description of the X-ray structure of Cu(DMAP)₄(BF₄)₂ proves that the DMAP ligands are coordinated to Cu(II) through the pyridine nitrogen atoms, in a tetragonal geometry.

Results of catalytic experiments

Having obtained an idea of the structure of the catalytically active complexes in solution, we will try to explain the results of the catalytic experiments, realizing that all measured reaction rates are in fact reoxidation rates of Cu(I) to Cu(II). In the following discussion, NO₃⁻ and BF₄⁻ will be considered as equivalent, non-coordinating counter-ions. Considering the strong resemblance of the catalytic and EPR results for both ions, this seems reasonable.

First Figs. 2 and 3 are reconsidered. From the results, it is concluded that OH^- and Cl^- counter-ions should be present simultaneously in order to obtain optimum catalytic activity, the optimum Cu:Cl:OH ratio being 1:1:1. An excess of OH^- poisons the catalyst drastically, but an excess of Cl^- counter-ions is less destructive, especially if $(\text{OH}/\text{Cu})_0 = 1$. Figure 1 should be examined with this in mind. It is obvious that the plots of R vs. DMAP/Cu for non-coordinating counter-ions level off at about DMAP/Cu = 4, irrespective of the presence of hydroxide (with $(\text{OH}/\text{Cu})_0 = 1$). From our spectroscopic studies, we already know that in these systems without initial OH^- addition the formation of mononuclear $\text{Cu}^{2+}(\text{DMAP})_4\text{X}_2^-$ (where $\text{X} = \text{BF}_4$ or NO_3) is nearly complete at DMAP/Cu = 4 (Fig. 8), whereas the transformation of dinuclear complexes into mononuclear complexes in the case of initially added OH^- (Fig. 10) levels off for DMAP/Cu > 4. The levelling off of R vs. DMAP/Cu can be explained in this way.

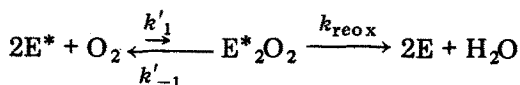
For coordinating Cl^- counter-ions the situation is completely different, and no levelling off of R vs. DMAP/Cu is observed (Fig. 1). Without initial hydroxide addition the transformation of dinuclear into mononuclear complex is by far incomplete, even at DMAP/Cu = 13 (Fig. 8). An increase in rate of oxidative coupling with increasing ligand/Cu ratio was more often observed [1, 4] and might be related to an enhancement in basicity of the reaction medium. This effect cannot be excluded for DMAP (see below), but for this strongly coordinating ligand the transformation into mononuclear complex might to a great extent be responsible for the observed acceleration. Thus, it seems likely that mononuclear complexes exhibit a higher catalytic activity than dinuclear complexes. This also allows us to explain the slight reduction in activity for $\text{Cl}/\text{Cu} > 1$ in Fig. 3. This reduction might be due to a transformation of mononuclear species into less active, probably dinuclear, ones with Cl^- as bridging ions (compare Table 3). The drop in Fig. 2 for $\text{OH}/\text{Cu} > 1$ can only partly be ascribed to the formation of dinuclear complexes with OH^- bridges (see Table 3, series VI). A more important reason, however, is the decomposition of the catalyst.

For the strong increase of R with DMAP/Cu > 4 shown in Fig. 1 for the system $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{OH}^- = 1:n:2:1$, another explanation is needed. From spectroscopic studies we learned that the enhancement of the concentration of mononuclear complexes is rather small for DMAP/Cu > 4 (Fig. 10), and so the strong increase of R with DMAP/Cu above this ratio cannot be due merely to an enhancement of the concentration of $\text{Cu}(\text{DMAP})_4^{2+}\text{X}_2^-$. It might be that in the case of the systems $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^- = 1:4:2$ and $\text{Cu}^{2+}:\text{DMAP}:\text{Cl}^-:\text{OH}^- = 1:4:2:1$, all coordination positions of the central copper ion are occupied with strongly coordinating DMAP ligands and Cl^- and/or OH^- counter-ions. The copper ion is hardly accessible to 2,6-dimethylphenol. A neutral DMP molecule can hardly compete with *e.g.* Cl^- and OH^- ions. Only when DMP is transformed into phenolate anion, *e.g.* by an excess of DMAP, this competition becomes significant. An increasing DMAP/Cu value leads to a higher basicity of the reaction medium, and this

enhances the phenolate anion concentration. A substitution as described above has been proposed by other authors [20, 21].

In the case of $\text{Cu}^{2+}:\text{DMP}:\text{NO}_3^- = 1:4:2$, $\text{Cu}^{2+}:\text{DMP}:\text{BF}_4^- = 1:4:2$ and $\text{Cu}^{2+}:\text{DMP}:\text{NO}_3^-:\text{OH}^- = 1:4:2:1$, non-coordinating counter-ions are present in the vicinity of Cu^{2+} . These loosely bound ions can easily be replaced by neutral DMP molecules, and an increase in the phenolate anion concentration by enhancing DMAP/Cu ratio is of no great advantage in this case.

Our major conclusion from the discussion above is the following: the catalytically most active species in our experiments is $\text{Cu}(\text{DMP})_4(\text{Cl})(\text{OH})$. It is obvious that, in spite of the fact that the overall reaction rate is determined by the reoxidation of Cu(I), R is increased on enhancing the concentration of the active species. It is clear that $k_2[\text{ES}]$ and $[\text{E}^*]$ are enhanced if $k_{2,\text{mono}} > k_{2,\text{di}}$ (see Scheme 2 with $\text{S} = \text{DMP}$). The same effect would be achieved for higher $[\text{DMP}]$. In Fig. 4, R is given as a function of $[\text{DMP}]$ for systems with almost only mononuclear species ($\text{Cu}^{2+}:\text{DMP}:\text{NO}_3^- = 1:4:2$), almost only dinuclear species ($\text{Cu}^{2+}:\text{DMP}:\text{Cl}^-:\text{OH}^- = 1:2:2:1$) and both kinds of species ($\text{Cu}^{2+}:\text{DMP}:\text{Cl}^- = 1:4:2$). For all three systems, it is demonstrated that for relatively low $[\text{DMP}]$ the reaction rate is first order in $[\text{DMP}]$. At higher $[\text{DMP}]$ ($\geq 0.04 \text{ mol dm}^{-3}$) the reoxidation of Cu(I) becomes rate determining and the strictly first-order dependence is lost. However, it is obvious that under these conditions it remains possible to accelerate the reaction by increasing $[\text{DMP}]$. In this case, $[\text{ES}]$ instead of k_2 is enhanced (see above) and again both $k_2[\text{ES}]$ and $[\text{E}^*]$ increase. Thus, the reoxidation rate will be influenced by factors preceding this step. According to Scheme 3, a higher value of $[\text{E}^*]$ will lead to a higher concentration of E^*O_2 and a higher reoxidation rate, $k_{\text{reox}}[\text{E}^*\text{O}_2]$. In Schemes 4 and 5 we indicated that the catalytically most active species for the oxidative coupling is mononuclear. However, this does not mean that E^* in Scheme 3 is also mononuclear. A deeper investigation of the dioxygen consumption as a function of the copper catalyst concentration was carried out (see Table 4). A plot of $^{10}\log R$ vs. $^{10}\log [\text{Cu}(\text{II})]$ shows an order in $[\text{Cu}(\text{II})]_0$ of approximately 2 (actually the order is 1.84). This implies that for the reoxidation step dimerization of Cu(I) complex is necessary, as shown purely schematically in Scheme 6.



Scheme 6.

This Scheme, in which E and E^* stand for Cu(II) and Cu(I) complex, respectively, deviates from the scheme proposed by Verlaan *et al.* (Scheme 3), who took insufficient account of the rate-limiting influence of the dioxygen diffusion from the gas phase for the case of high copper concentrations. For this reason they wrongly determined a first-order dependence in $[\text{Cu}(\text{II})]_0$ [1]. In view of Scheme 6, we now may comment on the role of Cl^- in the

TABLE 4

Dioxygen consumption rate R as a function of $[\text{Cu(II)}]_0$; standard conditions, except $[\text{Cu(II)}]_0$, with $\text{DMAP/Cu} = 4$ and $(\text{OH/Cu})_0 = 1$ (see experimental)

$[\text{Cu(II)}]_0$ (mmol dm^{-3})	R ($\text{mol dm}^{-3} \text{ s}^{-1}$)
0.83	14.1×10^{-6}
1.25	33.9×10^{-6}
1.66	59.0×10^{-6}
2.08	91.3×10^{-6}
2.49	116.7×10^{-6}
3.32	180.9×10^{-6}
3.74	216.4×10^{-6}

species $\text{Cu(DMAP)}_4(\text{OH})\text{Cl}$. The function of these bridging counter-ions is probably that of promoting the formation of dinuclear complexes which are necessary for the reoxidation of Cu(I) .

From the Δt measurements, it is clear that both Cl^- and OH^- should be present for rapid onset of the reaction. In this respect, one should keep in mind that the basicity of the DMAP ligands is rather high ($\text{pH} = 10.4$ in a 0.01 M solution of DMAP in demineralised water). Thus, it is likely that, when no copper-coordinating counter-ions are initially present, the dioxygen consumption does not begin until non-coordinated DMAP has produced some hydroxide out of traces of water present in the reaction mixture. For low DMAP/Cu values, the concentration of non-coordinated DMAP is negligible and Δt is very long. On increasing $[\text{DMAP}]$ in the reaction medium, the amount of unbound DMAP increases, the hydroxide production is faster and larger and Δt is shortened. Thus the catalytic activity of the complexes without initial hydroxide addition is explained. Cl^- counter-ions can take over the role of hydroxide to a certain extent. The fact that Δt is increased in going from $(\text{OH/Cu})_0 \cong 1$ to $(\text{OH/Cu})_0 = 2$ must be due to a partial transformation of the very active mononuclear complexes into less active dinuclear species (see the spectroscopic studies). Moreover the catalyst is decomposed (see earlier).

From the catalytic and spectroscopic experiments, it has already been concluded that a species $\text{Cu(DMAP)}_4\text{Cl(OH)}$ is the most active catalyst in the reaction medium. Thus, it is not surprising that Δt is minimum when the mentioned species is initially present.

Several investigators have claimed that catalytically active copper-amine species in the oxidative coupling of phenols are mononuclear [21 - 23]. According to others, many catalytically active species are dinuclear [10, 24 - 29]. In the present study it is shown that both species may act as catalysts, but the mononuclear complexes are the more active. Both species can be transformed into the other, the concentration of the most active mononuclear species depending on the nature of the copper counter-ions

and the DMAP/Cu value. A similar transformation has been reported by other authors [21, 30].

Finally, we briefly comment on the specificity of the catalyst. It is obvious that a higher basicity of the reaction medium is created on increasing DMAP/Cu, thereby favouring the formation of phenolate anions. In this way C—O coupling, leading to the desired PPO, is favoured [4]. On the other hand, an enhancement of [DMAP] makes the transformation of dinuclear species into mononuclear species more complete. Thus the presence of $\text{Cu}(\text{DMAP})_4\text{Cl}(\text{OH})$ together with the presence of phenolate anions seems favourable for PPO formation.

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