Synthesis Characterization of Heterodinuclear Co-Cu Complex and Its Electrocatalytic Activity towards O_2 Reduction Implications for Cytochrome *c* Oxidase Active Site Modeling

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A new dinucleating ligand consisting of a tetraphenylporphyrin derivative covalently linked with tris 2-benzimidazylmethyl - amine and its homodinuclear Co-Co and heterodinuclear Co-Cu complexes were synthesized and spectroscopically characterized. The heterobimetallic cobalt-copper complex bearing three benzimidazole ligands for copper as cytochrome *c* oxidase active site model was applied to the surface of glassy carbon electrode to show electrocatalytic activity for O_2 reduction in aqueous solution at an acidity level close to physiological pH value. The kinetic parameters of this electrocatalytic process were obtained.

Keywords   dinucleating ligand homodinuclear heterodinuclear cytochrome *c* oxidase structural model

Introduction

Metalloenzymes play many important roles in nature especially in electron-transfer biological processes. Because of their importance and complexity many simplified model systems have been constructed for the study of their chemistry. Among various polymetallicmetalloenzymes cytochrome *c* oxidase CcO is the one of the most special interest.

CcO the terminal enzyme of the respiratory chain catalyzes the reduction of O_2 by 4 H$^+$ 4 e$^-$ to water without leakage of any partially reduced intermediates which are toxic to cell such as H_2O_2. The free energy produced in this process is used to proton translocation and the electrochemical potential gradient generated by this proton pumping process is ultimately applied to drive the conversion of ADP to ATP.[1,2] X-Ray crystallographic studies[3-6] demonstrate that the O_2-binding/activating site in CcO consists of a myoglobin-type iron center heme a$_3$ and a copper atom Cu$_B$ coordinated to three histidine ligands.

With extensive study of many carefully designed functional analogues[7-37] of CcO considerable progress have been made in the elucidation of the catalytic mechanism of

O_2 reduction to water at the heterodinuclear heme a$_3$/Cu$_B$ site of CcO. However many issues remain controversial among which the role of the copper and the nature of the reaction intermediates in the catalytic process are the key subject of debate. Construction of artificial modeling systems of CcO will be essential and effective because this strategy may not only potentially answer the above issues about the mechanism but also allow the study of structure-catalytic activity relationships which in turn may lead to the design of efficient catalysts for the 4 e$^-$ reduction of O_2.

In this paper the synthesis and characterization of a porphyrin-tris 2-benzimidazylmethyl amine NTB dinucleating ligand Fig. 1 as well as a synthetic pathway leading to the corresponding homo and heterobimetallic complex of this ligand was described. The final Co-Cu complex as CcO active site model was applied to the surface of glassy carbon electrode to show electrocatalytic activity towards O_2 reduction in aqueous solution close to physiological pH.

Experimental

Materials and instruments

^{1}H NMR spectra were recorded on a Bruker AM-500 or a Varian-Mercury300 spectrometer and chemical shifts were reported relative to TMS and Ultraviolet-visible spectroscopy was performed using a Shimadzu UV-240 spectrophotometer. Elemental analyses C H and N were determined by Perkin-Elmer 240B elemental analyzer. An HP 7500a ICP-MS Agilent System was used for determination of metals. IR spectra were performed on a Shimadzu FT-IR-8100 spectrometer KBr pellets . MS spectra were recorded on a Finnigan LCQ ESI-MS spectrometer or a ZAB-HF-3F MS instrument. X band ESR spectra were
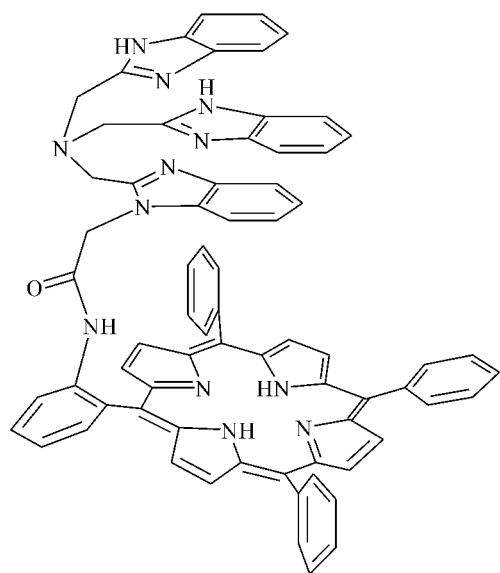
Fig. 1   Proposed structure of the dinucleating ligand.

recorded on an ER 200-D-SRC 1012 spectrometer. Electrochemical experiments were performed on a CHI model 660A electrochemical workstation with a three-electrode system using glassy carbon electrode GCE as working electrode   Pt wire as counter electrode and saturated

calomel electrode   SCE   as reference electrode. GCE 3 mm in diameter   procured from Bioanalytical Systems was polished using alumina powder and then cleaned ultrasonically in a $HNO_3 + H_2O$ mixture 1:1 V/V absolute alcohol   and doubly distilled water   sequentially. Modification of the GCEs was achieved by immersing the electrode surface into a freshly prepared solution in CH_2Cl_2 approximately 5×10^{-4} mol L^{-1} for 5 min and dried in air. O_2 gas with 1.01×10^5 Pa pressure was bubbled into pH 6.8 buffer solutions of Na_2HPO_4-NaH_2PO_4 throughout the electrocatalytic experiment.

DMF was dried over 4 Å molecular sieves and redistilled under Argon. Pyrrole was purchased from Fluka and redistilled prior to use. All other chemicals were purchased from commercial sources and used as received without further purification. NTB was prepared according to the literature[38] procedure. The preparation of 5- *o*-aminophenyl -10 15 20-triphenylporphyrin was made using the method described in literature.[39]

Synthesis

The synthetic route to the final Co-Cu model complex is outlined in Scheme 1.

Scheme 1   Synthetic route to the Co-Cu complex **7**. Large ellipses represent porphyrin ellipses containing N NTB moiety
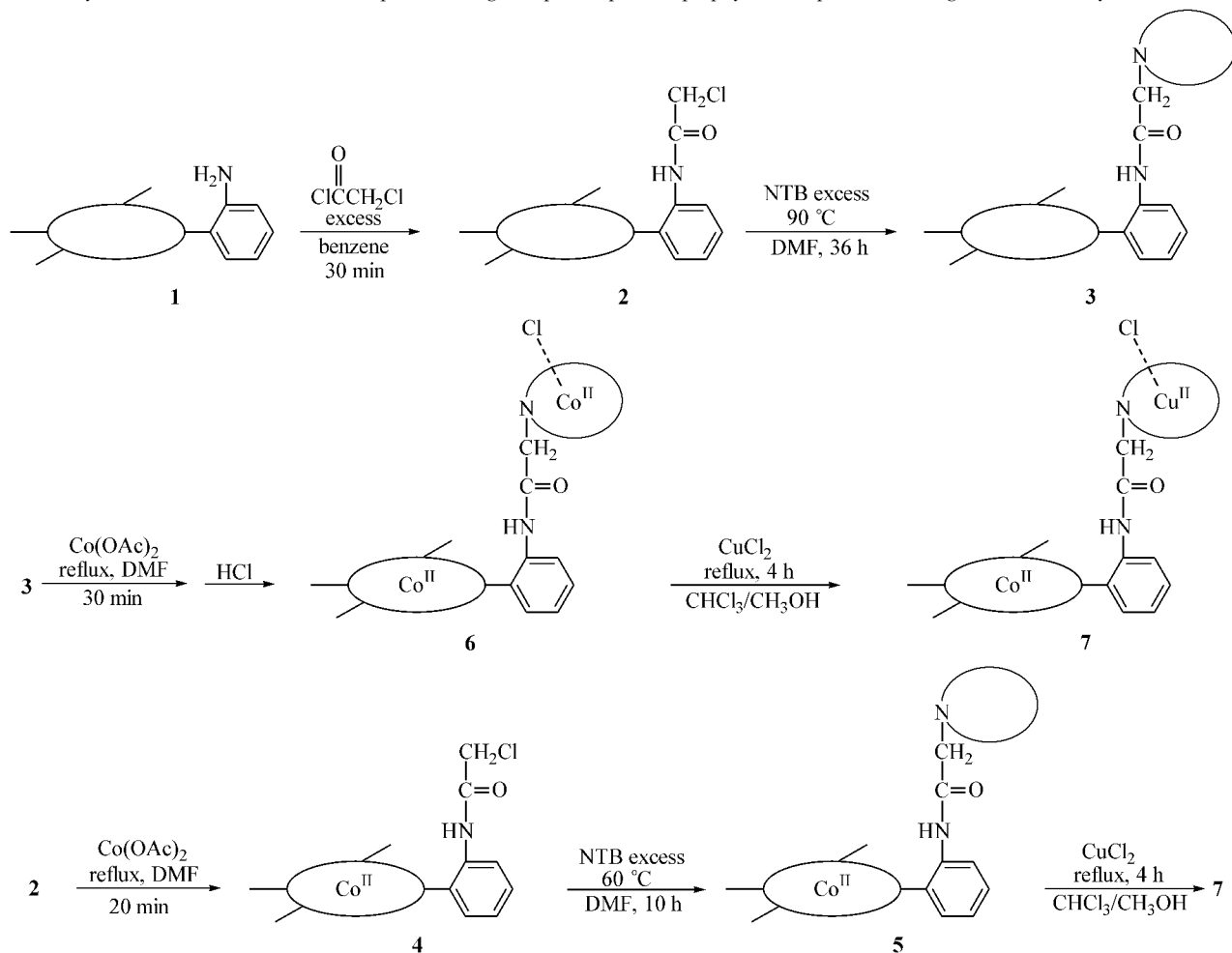
Synthesis of the precursor **2**   A solution of 5- *o*-aminophenyl -10 15 20-triphenylporphyrin **1** 157 mg 0.25 mmol in benzene 80 mL was brought to reflux then a solution of chloroacetyl chloride 0.1 mL 1.25 mmol in benzene 5 mL was added dropwise to the mixture within a 10 min period. The reaction mixture was stirred under reflux for another 30 min cooled washed with saturated aqueous sodium carbonate dried over anhydrous sodium sulfate and filtered. Upon removal of the solvent in the filtrate the desired compound was obtained. After further purification by recrystallization from $CHCl_3$-CH_3OH the precursor was obtained in 70% yield. UV-vis $CHCl_3$ λ_{max} 420 512 546 585 647 nm ^{1}H NMR $CDCl_3$ 300 MHz δ 8.88—8.76 m 8H H_β 8.26—8.18 m 6H H_{aro} 8.08 d $J = 6.9$ Hz 2H H_{aro} 7.86—7.76 m 9H H_{aro} 7.59 t 2H H_{aro} 3.43 s 2H CH_2 – 2.72 s 2H pyrrole NH IR KBr ν 3317 3047 2910 2843 1676 1614 1521 1467 1441 1344 cm^{-1} MS ESI m/z 705.2 M$^+$.

Synthesis of the dinucleating Ligand **3**   **2** 141 mg 0.2 mmol NTB 407 mg 1 mmol anhydrous potassium carbonate 200 mg were thoroughly mixed in 40 mL of DMF. The reaction mixture was stirred at 90 ℃ for 36 h under N_2 then concentrated to a smaller volume under reduced pressure and poured into 50 mL of distilled water. After filtration the precipitate was dried overnight under vacuum and dissolved in a minimum amount of $CHCl_3$ and was chromatographed on a column of silica gel using a solvent mixture of $CHCl_3$-CH_3OH 9:1 V/V as eluent. The second band eluted off the column was collected and the solvent was evaporated. The residue was recrystallized from CH_2Cl_2-CH_3OH to afford the dinucleating ligand **3** 118 mg in 55% yield. UV-vis $CHCl_3$ λ_{max} 244 275 282 420 517 552 588 646 nm ^{1}H NMR $CDCl_3$ 500 MHz δ 9.14 d $J = 8.0$ Hz 2H H_β 8.87—8.68 m 6H H_β 8.54 d $J = 7.8$ Hz 1H H_{aro} 8.31—8.19 m 6H H_{aro} 8.06 d $J = 7.8$ Hz 1H H_{aro} 7.89—7.76 m 10H H_{aro} 7.52—7.40 m 7H H_{aro} 7.07—6.95 m 6H H_{aro} 3.58 s 6H $3CH_2$ 1.59 s 2H CH_2 coincident with solvent peak – 2.77 s 2H pyrrole NH IR KBr ν 3311 3051 2920 2852 1664 1599 1533 1438 cm^{-1} MS ESI m/z 1077.4 M$^+$ + H . Anal. calcd for $C_{70}H_{52}N_{12}O$ C 78.07 H 4.83 N 15.61 found C 77.80 H 5.15 N 15.29.

Synthesis of compound **4**   Preparation of **4** was accomplished by refluxing porphyrin **2** and 10 equiv. of cobalt acetate in DMF until UV-vis spectroscopy indicated completion of the reaction. UV-vis $CHCl_3$ λ_{max} 410 527 nm IR KBr ν 3048 2923 2853 1687 1580 1523 1445 1001 cm^{-1}.

Synthesis of compound **5**   Under N_2 gas **4** 152 mg 0.2 mmol NTB 407 mg 1 mmol anhydrous potassium carbonate 200 mg were thoroughly mixed in 40 mL of DMF. The reaction mixture was stirred at 60 ℃ for 10 h then concentrated to a smaller volume under re-

duced pressure and poured into 50 mL of distilled water. After filtration the precipitate was dried overnight under vacuum and dissolved in a minimum amount of $CHCl_3$ and was directly loaded onto a column of silica gel eluted with a mixture of $CHCl_3$-EtOH 11:1 V/V . The main red band eluted off the column was collected and the solvent was evaporated and the residue was recrystallized from CH_2Cl_2-EtOH to give **5** 152 mg 67% . UV-vis $CHCl_3$ λ_{max} 247 276 283 411 547 nm IR KBr ν 3319 3053 2924 2853 1657 1578 1533 1446 1004 cm^{-1} MS ESI m/z 1134.2 M$^+$ + H 686 CoTPP + NH 407 NTB . Anal. calcd for $CoC_{70}H_{50}N_{12}O\cdot 2H_2O$ C 71.86 H 4.62 N 14.37 found C 71.80 H 4.92 N 14.59.

Synthesis of the homodinuclear complex **6**   **3** 107.6 mg 0.1 mmol cobalt acetate 249 mg 1 mmol in DMF 20 mL were refluxed for 30 min under N_2 gas. When cooled the mixture was poured into 1 mol L^{-1} dilute hydrochloric acid 100 mL . After filtration the precipitate was dried overnight under vacuum and dissolved in a minimum amount of $CHCl_3$ and chromatographed on a column of silica gel with a mixture of $CHCl_3$-CH_3OH 9:1 V/V as eluent. The first red band eluted off the column was collected and the solvent was evaporated under vacuum. The residue was recrystallized from $CHCl_3$-CH_3OH to provide **6** 110 mg 90% . UV-vis $CHCl_3$ λ_{max} 240 413 526 nm IR KBr ν 3319 3051 2921 2851 1657 1598 1533 1446 1004 cm^{-1} MS FAB m/z 1227 M$^+$ 1229 M$^+$ + 2 1192 M − Cl 466 NTB + Co 670 CoTPP − H 686 CoTPP + NH 713 CoTPP + NH + CO − H 727 CoTPP + NH + CO + CH_2 − H . Anal. calcd for $Co_2C_{70}H_{50}N_{12}ClO\cdot 2H_2O$ C 66.48 H 4.27 N 13.30 Co 9.34 found C 66.67 H 4.48 N 13.67 Co 9.07.

Synthesis of the heterodinuclear complex **7**   **5** 113 mg 0.1 mmol was dissolved in 20 mL of $CHCl_3$ then a solution of cupric dichloride 69 mg 0.4 mmol in 10 mL of methanol was added. After the mixture was stirred under reflux for 4 h the solvent was removed under reduced pressure to form a solid which was washed with dilute hydrochloric acid and distilled water to remove excess $CuCl_2$ and dried under vacuum. The resulting residue was dissolved in CH_2Cl_2 and purified by chromatography on a silica gel column with CH_2Cl_2-CH_3OH 7:1 V/V as eluent. The red fraction was collected and evaporated to dryness to give the heterodinuclear complex **7** 106 mg 86% yield .

The heterodinuclear complex **7** could be obtained from an alternative method. For a typical procedure to a solution of **6** 61 mg 0.05 mmol in $CHCl_3$ 15 mL a solution of cupric dichloride 43 mg 0.25 mmol in 5 mL of methanol was added. The mixture was stirred for 4 h under reflux. The following procedure was the same as described above to afford **7** in 96% yield. UV-vis $CHCl_3$ λ_{max} 240 414 428 539 641 nm IR KBr ν 3320 3053 2922 2851 1654 1577 1530 1448 1003

cm^{-1} MS FAB m/z 1231 M^+ 1233 $M^+ + 2$ 1197 $M^+ - Cl + H$ 470 NTB + Cu 670 CoTPP – H 686 CoTPP + NH 713 CoTPP + NH + CO – H . Anal. calcd. for $CoCuC_{70}H_{50}N_{12}ClO$ H_2O C 67.23 H 4.16 N 13.45 Co 4.72 Cu 5.16 found C 67.57 H 3.98 N 13.29 Co 4.83 Cu 4.67.

Results and discussion

Synthesis

Heterobimetallic complexes have received considerable attention because of their potential in modeling the structures and reactivities of metalloenzymes containing two different metal ions in their active sites. Here the final Co-Cu heterodinuclear complex **7** could be obtained by two parallel routes Scheme 1 one condensation of the precursor **2** with NTB in DMF under the presence of anhydrous K_2CO_3 afforded the free base **3** bearing two different coordination sites then metalation of **3** with excess cobalt acetate gave the homodinuclear Co-Co complex **6** followed by metathesis of the cobalt in NTB moiety with copper to afford the heterodinuclear Co-Cu complex **7** the other coupling of the metalated precursor **4** with NTB under the same condition within much shorter period afforded the mononuclear CoPor-NTB compound **5** bearing only one coordination site which was further metalated by cupric dichloride to give the final complex. The results of MS IR UV spectra and elemental analyses as well as thin layer chromatography showed that the two different routes led to the same complex.

In the course of stepwise metalation of the free base **3** our initial attempt to remove the cobalt coordinated to the NTB moiety in complex **6** by washing with dilute hydrochloric acid failed. To our surprise it was found that the cobalt in **6** could be easily substituted with copper by refluxing **6** with an excess of cupric dichloride in a mixture of $CHCl_3/CH_3OH$ to give the final complex.

^1H NMR *spectrum*

The NTB moiety methylene groups of the dinucleating ligand **3** appear in the ^1H NMR spectrum at δ 3.58 upfield shifted relative to the corresponding signal in NTB at δ 4.12. Phenyl protons in NTB moiety of **3** showing peaks at δ 7.46 and 7.04 were also upfield shifted compared with those of NTB itself located at δ 7.60 and 7.19 in DMSO.[38] This change in ^1H NMR suggests an important interaction between the porphyrin core and NTB moiety.

UV-vis *spectrum*

The electronic spectra of compounds **3** **5** **6** and **7** and the spectral data of them are shown in Fig. 2 and Table 1. It can be clearly seen that the electronic absorption spectra of complex **3** and **5** both show relatively strong absorption in the region of 240—300 nm. Nevertheless after the insertion of Co or Cu into the NTB moiety in complexes **6** and **7** the three peaks in this region reduced to only one sharp peak at $\lambda = 240$ nm. The change of the absorption peaks in this region implicated the successful insertion of Co and Cu into the NTB moiety of **6** and **7**. Furthermore compared with **5** whose Q band is located at 547 nm the Q bands of **6** 526 nm and **7** 539 nm both show blue-shift. This shift implies an interaction between the two metals located in NTB moiety and in the porphyrin core and furthermore the difference between interaction of Co-Co and Co-Cu.

MS *spectrum*

In the MS spectra of complexes **6** and **7** the observed peaks were in well accordance with the expected ones. It was found that this two spectra exhibited molecular ion peaks at the mass number $m/z = 1231$ and 1227 corresponding to CoPor-NTBCuCl and CoPor-NTBCoCl respectively. Furthermore this two complexes gave an additional MS peak at $m/z = 1197$ and 1192 probably due to the loss of the chloride anion which was assigned to be CoPor-NTBCu $^+$ and CoPor-NTBCo $^+$ respectively. It should be noted that complex **6** was obtained by metalation of the dinucleating ligand **3** with cobalt acetate followed by washing with dilute hydrochloric acid thus the chloride anion in **6** may be introduced by this washing process. Furthermore in consideration of the abundance of chlorine isotopes and the mode of the observed molecular ion peaks the species coordinated to Co and Cu in NTB moiety of **6** and **7** should be chloride anion Scheme 1 .

ESR *spectroscopy*

Efforts in preparing single crystal sample of the Co-Cu complex **7** in order to get detailed information about the coordination geometry at Cu II failed and the ESR spectrum of the Co-Cu complex was too complicated to interpret possibly due to an overlapping of the ESR signals of these two Co II and Cu II paramagnetic metals. To obviate this problem an analogous sample of **7** Zn II Por-NTB-Cu II Cl was prepared according to the similar synthetic route and applied to ESR spectroscopy. Fig. 3 shows the ESR spectrum of complex Zn II Por-NTBCu II Cl in $CHCl_3$ at 103 K from which the well-defined ESR parameters $g_{//} = 2.04$ $g_{\perp} = 2.17$ and $A_{//} = 108$ G were obtained. Such parameters strongly indicate that the Cu II ion in complex Zn II Por-NTBCu II Cl has a trigonal-bipyramidal environment following the criteria given by Bencini *et al*.[40] Zinc is not cobalt but its introduction would not result in a change of coordination mode of the copper in NTB moiety. So combined with the above MS spectra information of complex **7** it can be concluded that copper in NTB moiety of **7** is five coordinated that is to say in complex **7** copper is coordinated to four tertiary nitrogen atoms and one chloride anion Fig. 4 .
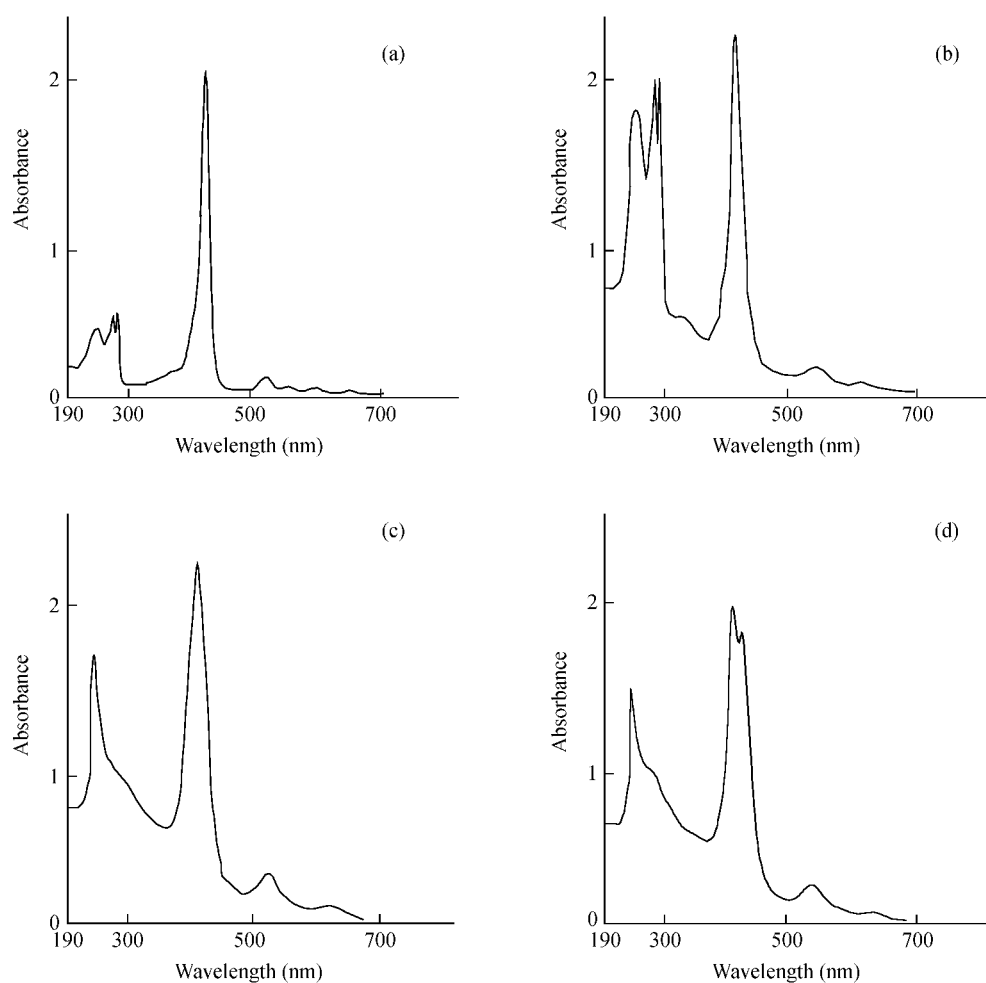
Fig. 2 UV-vis spectra of compounds **3** **5** **6** and **7** in chloroform in the region of 190—700 nm. a **3** Por-NTB dinucleating ligand b **5** CoPor-NTB c **6** CoPor-NTBCoCl d **7** CoPor-NTBCuCl.

Table 1 Spectral data of the compounds in CHCl$_3$

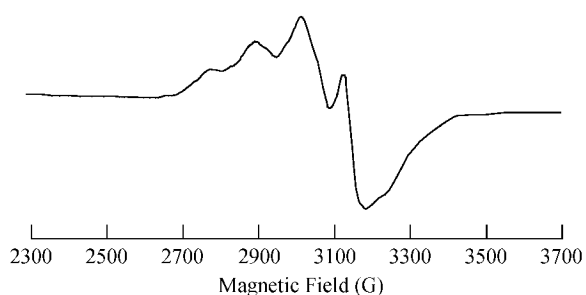| Compound	Soret nm	ε L mol^{-1} cm^{-1}	Q nm	ε L mol^{-1} cm^{-1}						
3	420	94060	517	6560	552	3280	588	2630	646	2190
5	411	105000			547	8970	615	4380		
6	413	102000			526	14320	621	5430		
7	414	89690	428 83130		539	10500	641	3060		

Fig. 3 ESR spectrum of ZnPor-NTBCuCl 0.3 mmol L^{-1} at 103 K in CHCl$_3$. Microwave frequency 9.45 GHz modulation width 2 Gauss microwave power 1 mW.
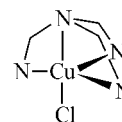

Fig. 4 Coordination geometry of Cu II to NTB moiety in complex **7**.

Electrochemical reduction of O$_2$ *on* GCE *modified by the* Co-Cu *complex* **7**

To check the feasibility of the heterodinuclear Co-Cu complex as CcO active site model the cyclic voltammo-

grams of O_2 reduction at GCE modified with it were studied. It should be noted that NTB is a ligand which can form stable complexes with many transition metals so it was chosen by us for the synthesis of the desired model compound in order to ensure the copper will retain when it is adsorbed on the surface of electrodes. This is of considerable importance in the study of the role of copper in O_2 reduction as stated by Boitrel *et al*.[37] And in fact this Co-Cu complex **7** shows high stability during multiple CV scans and the *I-E* profile obtained in the first scan is very similar to those in subsequent scans. Fig. 5 depicts the cyclic voltammograms of GCE modified with the Co-Cu complex under different conditions. It can be clearly observed that in oxygen saturated solution the catalytic current increases apparently relative to that in air saturated and deoxygenated solutions. Furthermore the peak current of the modified electrode is 1.4 times as high as that obtained at an unmodified electrode and the peak potential of O_2 reduction shifts positively by about 170 mV and is located at -0.67 V vs. SCE Fig. 6 . This phenomenon demonstrates that the Co-Cu complex shows electrocatalytic activity towards O_2 reduction at an acidity level close to physiological pH value.
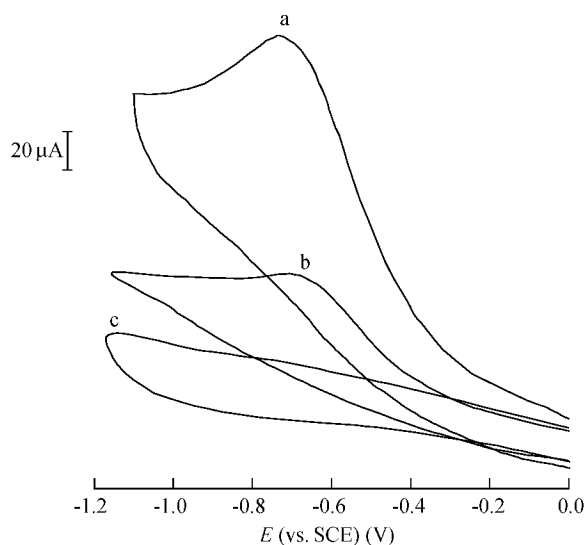

Fig. 5 Cyclic voltammograms of O_2 reduction at GCE modified with **7** at a scan rate of 100 mV/s in a oxygen saturated b air saturated and c deoxygenated pH 6.8 buffer solution.

Dioxygen can reduce at the chemically modified electrodes by a $2e^-$ process to H_2O_2 or via a direct $4e^-$ reduction to H_2O. The current of oxygen reduction on GCE modified by the Co-Cu complex **7** increased with the increase of scan rate Fig. 7 . Plot of reduction peak currents vs. scan rate $^{1/2}$ for oxygen reduction is given in Fig. 8. This excellent linearity indicates that the electrocatalytic process is controlled by O_2 diffusion. For a typical irreversible reaction the relationship between peak current and scan rate is as follows[41]
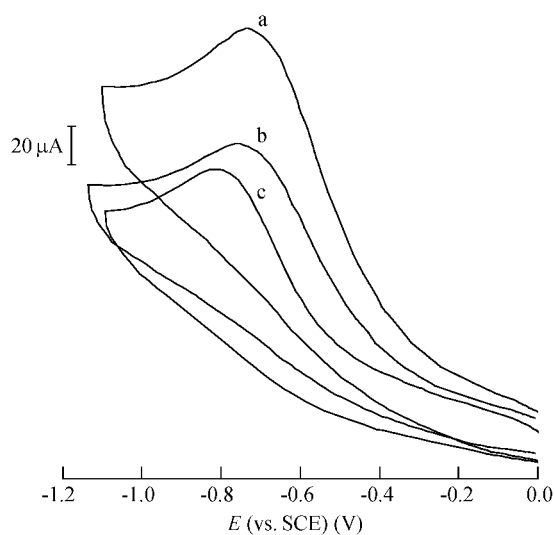

Fig. 6 Cyclic voltammograms of O_2 reduction at a scan rate of 100 mV/s in an oxygen saturated buffer solution of pH = 6.8 at bare GCE c GCE modified with complex **5** b and GCE modified with Co-Cu complex **7** a .
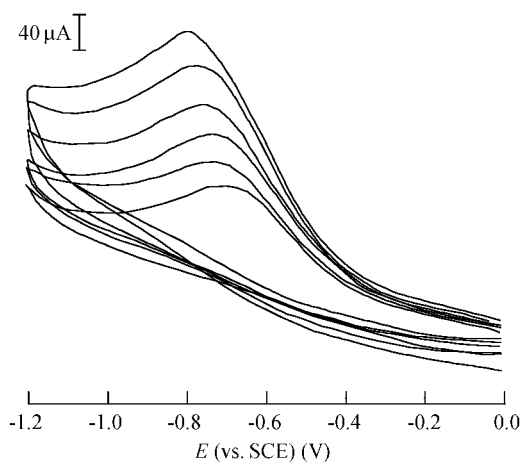

Fig. 7 Cyclic voltammograms of O_2 reduction on GCE modified by **7** at different scan rates in pH = 6.8 buffer solution. From top to bottom the scan rate is 300 250 200 150 100 and 50 mV/s respectively.
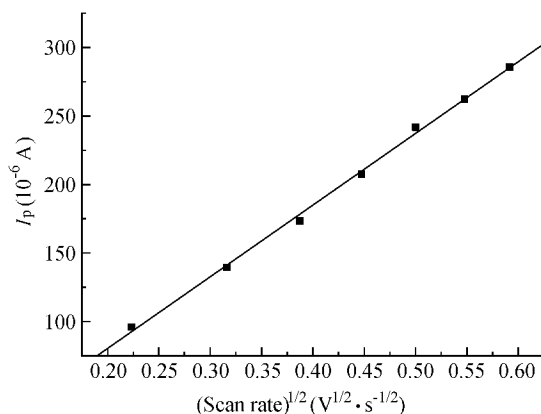

Fig. 8 Plot of reduction peak currents vs. scan rate $^{1/2}$ obtained from CVs at GCE modified with **7** in pH = 6.8 buffer solution.

$$I_P = 0.4958nFAC_o^* \quad \alpha n_a F/RT^{1/2} \nu^{1/2} D_o^{1/2} \qquad 1$$

$$E_P - E_{P/2} = -1.857RT/\alpha n_a F \qquad 2$$

where I_P　n　α　n_α　A　C_o^*　D_o and ν represent the peak current　the number of electrons transferred　the transfer coefficient　the apparent number of electrons involved in the rate determining step　the electrode area　the bulk concentration　the oxygen diffusion coefficient and the scan rate　respectively. In the same oxygen saturated buffer solution　$C_o^* D_o^{1/2}$ is determined by Hu et al.[42] to be 3.6×10^{-9} mol s$^{-1/2}$ cm^{-2}. In the present experiment　the difference between the peak potential　E_p　and the half-wave potential　$E_{P/2}$　remains constant as approximately 180 mV. From the above two equations　αn_α and the number of the changed electrons n for the reduction are calculated to be 0.26 and 3.4—3.5 respectively. This means that the $2e^-$ and $4e^-$ reduction mechanisms occur simultaneously but much of the O_2 reaching the electrode by diffusion is reduced through the $4e^-$ mechanism. The compound **5**　which contains no copper　was also checked for its catalytic activity towards O_2 reduction using the above procedure for **7** and the number of the changed electrons is only 2.2 under the same condition　Fig. 6 . From this comparison between the Co and Co-Cu complexes and the fact that the Co-Cu compound is more efficient than **5** in O_2 reduction　it is suggested that copper may play an important role in the cycle of O_2 reduction as described by Collman et al.[28-30]

Conclusions

In conclusion　a new ligand bearing two different co-ordination sites was synthesized and characterized　its homodinuclear and heterodinuclear complexes were also prepared and characterized. The heterodinuclear Co-Cu complex　served as CcO active site model　was characterized by IR　UV-vis　MS and ESR spectroscopy as well as elemental analysis. It was applied to the surface of glassy carbon electrode to show electrocatalytic activity towards O_2 reduction by a mixed $2e^-/4e^-$ mechanism in aqueous solution near the physiological pH. Preparation of other model compounds of CcO with these two components by changing the chain length of the linker molecule between them to obtain a $4e^-$ catalyst for O_2 reduction is under investigation.

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