NJC

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Table of Contents

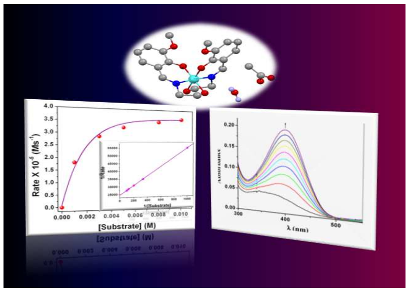
A mononuclear cobalt(III) complex and its catecholase activity

Merry Mitra,[a] Pallepogu Raghavaiah[b,c] and Rajarshi Ghosh*[a]

[a] *Department of Chemistry, The University of Burdwan, Burdwan 713 104, India.*
Fax: +91-342-2530452; Tel: +91 342 2533913 ext: 424; E-mail:
rajarshi_chem@yahoo.co.in.
[b] *Department School of Chemistry, University of Hyderabad, Hyderabad 500 046, India*
[c] *Present address: Department of Chemistry, Dr. Harisingh Gour University, Sagar 470 003, India*

Graphical Abstract

A mononuclear Co(III) complex is mimicking the catechol oxidase enzyme with appreciably high turnover numbers in different solvents.



Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

A mononuclear cobalt(III) complex and its catecholase activity

Merry Mitra,[a] Pallepogu Raghavaiah[b,c] and Rajarshi Ghosh*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Structural analysis of a cobalt(III) complex $[Co(HL)_2](OAc).H_2O$ (**1**) [H_2L = *N*-(2-hydroxyethyl)-3-methoxysalicylaldimine] reveals tridentate chelation behaviour of the ligand H_2L having a distorted octahedral coordination environment around the cobalt(III) center with a CoN_2O_4 chromophore. **1** behaves as an effective catalyst towards oxidation of 3,5-di-*tert*-butylcatechol in different solvents, *viz.* dichloromethane (DCM), methanol (MeOH) and acetonitrile (MeCN) to its corresponding quinone derivative in aerial oxygen. The reaction follows Michaelis-Menten enzymatic reaction kinetics with turnover numbers (K_{cat}), 1.46×10^3, 1.21×10^3 and 2.16×10^3 h^{-1} in DCM, MeOH and MeCN, respectively.

Introduction

In plant system, catalysis of oxidation of *o*-diphenol (catechol) to corresponding quinone coupled with $2e/2H^+$ reduction of oxygen to water, in presence of molecular oxygen is known as catecholase activity. The resulting quinones autopolymerize to give brown pigments which are responsible to defense the damage caused by the pathogens and insects in plants. The crystal structure of the *met* form of the enzyme catechol oxidase, also known as *o*-diphenol oxidase, contains two hydroxobridged strongly antiferromagnetically coupled copper(II) centres in their active site. The each copper(II) centre is coordinated to three histidine nitrogens and adopts a trigonal pyramidal environment with one nitrogen in the apical site. Since the elucidation of its crystal structure[1] several reports of dicopper(II) complexes have been found[2-5] to correlate the structure-function relationship of this biocatalytic reaction. Moreover, different monocopper(II),[6] manganese(III),[6e,7] nickel(II),[8] nickel(II)-manganese(II),[9] Fe(III),[10] cobalt(II/III)[11] and zinc(II)[12] compounds are available which show catecholase activity. All these indicate that the exploration of the possibility of catecholase activity by new types of species with different ligand environment, and different metal ions along with their different oxidation state(s) and nuclearity, that can mimic the native enzyme, deserves special importance. The exact structure-property correlation for catecholase activity is yet to be appeared indicating the necessity of modeling catecholase active complexes. Here, in this endeavor, we report the synthesis and characterization of a mononuclear cobalt(III) complex (**1**),[13] with an (N,O) donor Schiff base ligand and its catalytic activity towards oxidation of a catechol derivative to its corresponding quinone in different solvents.

Experimental

Materials

High purity *o*-vanillin (Aldrich, UK), 2-aminoethanol (Aldrich, UK), cobalt(II) acetate tetrahydrate (Aldrich, UK), 3,5-di-*tert*-butylcatechol (Aldrich, UK) and all other solvents were purchased from the respective concerns and used as received. Solvents were dried according to standard procedure and distilled prior to use.

The ligand H_2L [H_2L = *N*-(2-hydroxyethyl)-3-methoxysalicylaldimine] was prepared using a reported procedure.[14] *O*-vanillin (0.3043 g, 2 mmol) was heated under reflux with 2-aminoethanol (0.1222 g, 2 mmol) in 30 ml dehydrated ethanol. After 2 h, the reaction solution was evaporated under reduced pressure to yield a yellow coloured solid, which was dried under vacuum and stored over $CaCl_2$ for subsequent use.

For catecholase activity study, 1×10^{-4} mol dm^{-3} solution of **1** (0.0005 g) was treated with 1×10^{-2} mol dm^{-3} (100 equivalents) of 3,5-DTBC (0.0222 g) under aerobic conditions.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. UV-Vis and IR spectra (KBr discs, 4000-300 cm^{-1}) were recorded using a Shimadzu UV-Vis 2450 spectrophotometer and Perkin-Elmer FT-IR model RX1 spectrometer, respectively. The H^1 NMR spectral data were collected in $CDCl_3$ on a Bruker 400 MHz spectrometer. Mass spectrometric data were collected on

---

[a] *Department of Chemistry, The University of Burdwan,
Burdwan 713 104, India. Fax: +91-342-2530452;
Tel: +91 342 2533913 ext: 424; E-mail: rajarshi_chem@yahoo.co.in.*
[b] *Department School of Chemistry, University of Hyderabad, Hyderabad 500 046, India.*
[c] *Present address: Department of Chemistry, Dr. Harisingh Gour University, Sagar 470 003, India*

† Electronic Supplementary Information (ESI) available: [magnetic and spectroscopic plots are included here]. See DOI: 10.1039/b000000x/

Xevo G2 Q TOF mass spectrometer.

Preparation of 1

A methanolic solution (5 cm^3) of $Co(OAc)_2.4H_2O$ (0.0623 g, 0.25 mmol) was added dropwise to a stirring solution of H_2L (0.0244 g, 0.125 mmol) in DCM (10 cm^3). The brown solution with reddish tinge was filtered and the supernatant liquid was kept in air for slow evaporation. The product was obtained as square deep brown solid.

Yield: (based on metal salt) 0.1126 g (86.22%). *Anal*. calc. for $C_{22}H_{27}N_2O_9Co$ (**1**): C, 50.58; H, 5.21; N, 5.36; Found: C, 50.32; H, 4.90; N, 4.92. Selected IR bands (KBr pellet, cm^{-1}): 3461 (s), 1655 (s), 1648 (s), 973 (s). UV-Vis (λ, nm): 252, 390, 495 and 751.

X-ray diffraction study

Single crystals of **1** suitable for X-ray crystallographic analysis was selected following examination under a microscope. Diffraction data was collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) and was identified as $P\ 2_1/c$ space groups. The crystal data and refinement details are listed in Table 1. The structure was solved by direct methods, and the structure solution and refinement were based on $|F|^2$. The final differences Fourier map showed the maximum and minimum peak heights at 0.575 and -0.364 $eÅ^{-3}$ with no chemical significance. All calculations were carried out using SHELXL-97[15] and were refined using SHELSL-97.[15] All the figures have been generated using ORTEP-32.[16]

Table 1 Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{22}H_{27}N_2O_9Co$
Formula weight	522.39
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å))	15.959(5)
b (Å)	11.194(3)
c (Å)	13.281(4)
α (°)	90.00
β (°)	100.678(5)
γ (°)	90.00
V ($Å^3$)	2331.4(12)
Z	4
D_{calc} (mg/m^3)	1.488
Absorption coefficient (mm^{-1})	0.791
F(000)	1088
Crystal size (mm^3)	0.36×0.21×0.09
Theta range for data collection (°)	1.30-25.97
Index ranges	$-19 \leq h \leq 19$, $-13 \leq k \leq 13$, $-16 \leq l \leq 16$
Reflections collected	23447
Independent reflections	4563 [R_{int} = 0.0356]
Completeness to theta	99.8% (θ = 25.97)
Absorption correction	Multi-scan
T_{max} and T_{min}	0.9322 and 0.7638
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4563/2/318
Goodness-of-fit (GOF) on F^2	1.063
Final R indices [l > 2σ(l)]	R1 = 0.0556, wR_2 = 0.1456
R indices (all data)	R1 = 0.0672, wR_2 = 0.1542
Largest difference in peak and hole(e $Å^{-3}$)	0.575, -0.364

Results and Discussion

Synthesis and formulation

Complex **1** was synthesized by addition of methanolic solution of Co(II) acetate tetrahydrate into the dichloromethane solution of the ligand H_2L.

The compound was characterized using elemental analysis, IR, UV, NMR and single crystal X-ray crystallography. IR spectrum of **1** shows relatively intense peaks around 1590–1600 cm^{-1} due to the C=N stretching frequency and weak bands in the range 2980–2900 cm^{-1} due to the aliphatic C–H stretching.

X-ray structure

The molecular structure of **1** is shown in Fig. 1. X-ray crystallography reveals (Table 1) that the hexacoordination around the Co(III) centre is completed by the N and O donor centres from each of the organic ligand frameworks.

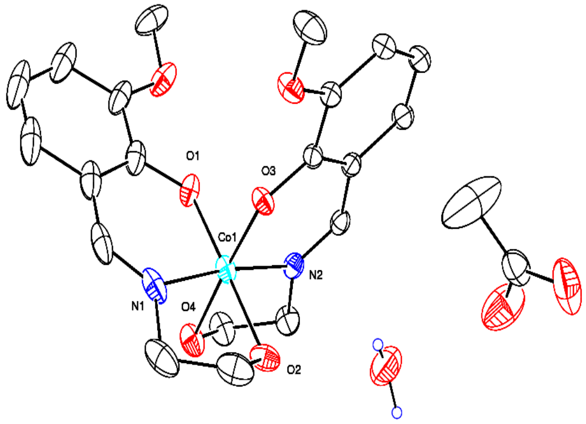


Fig. 1 ORTEP diagram of **1** with 20% ellipsoid probability plot.

The diamagnetic behavior (Fig. S1; Supporting Information) as well as comparison of the bond angle-bond distance parameter (Table 2) of the complex with other reported ones confirms the oxidation state of the metal as +III. The phenolic OH in the ligand framework gets deprotonated[13] because of its higher acidity than alcoholic OH, hence the monocationic $[Co(HL)_2]^+$ is being formed. The positive charge of the complex is neutralized by a crystallized acetate anion. The geometry around metal(III) centre is best described as distorted octahedron. Bond angle and bond distance data (Table 2) reveal that the phenolic oxygen O1 and the alcoholic oxygen O2 are at the axial position of the octahedron. The rest N1, N2 (imine nitrogens) and O3 (phenolic oxygen), O4 (alcoholic) are at axial position.

Table 2 Bond lengths [Å] and angles [°] for **1**.

Bond lengths			
Co(1)-O(1)	1.856(2)	Co(1)-O(4)	1.952(3)
Co(1)-O(2)	1.945(3)	Co(1)-N(1)	1.891(3)
Co(1)-O(3)	1.875(2)	Co(1)-N(2)	1.887(3)
Bond angles			
O(1)-Co(1)-O(2)	178.46(11)	O(2)-Co(1)-N(2)	90.07(11)
O(1)-Co(1)-O(3)	91.56(11)	O(3)-Co(1)-O(4)	177.08(11)
O(1)-Co(1)-O(4)	91.28(12)	O(3)-Co(1)-N(1)	89.47(11)
O(1)-Co(1)-N(1)	95.11(14)	O(3)-Co(1)-N(2)	95.12(10)
O(1)-Co(1)-N(2)	89.62(10)	N(1)-Co(1)-O(4)	90.93(12)
O(2)-Co(1)-O(3)	89.97(10)	N(1)-Co(1)-N(2)	173.33(13)
O(2)-Co(1)-O(4)	87.18(12)	N(2)-Co(1)-O(4)	84.25(11)
O(2)-Co(1)-N(1)	85.08(14)		

Catecholase activity of 1: Spectrophotometric study

In order to study the catecholase activity of the complex **1**; 3,5-DTBC with two bulky *t*-butyl substituents on the ring and low quinone-catechol reduction potential has been chosen as substrate. This makes it easily oxidized to the corresponding *o*-quinone, 3,5-DTBQ which is highly stable and shows a maximum absorption at 401 nm in DCM. Solution of **1** was treated with 100 equivalents of 3,5-DTBC under aerobic conditions. The repetitive UV-Vis spectral scan was recorded in pure DCM (Fig. 2). Spectral bands at 751, 495, 390 and 252 nm appeared in the electronic spectrum of complex **1**, whereas 3,5-DTBC showed a single band at 282 nm. After addition of 3,5-DTBC, the time dependent spectral scan showed very smooth growing of quinone band at 401 nm, as reported by Krebs *et al*,[17] which indicated the formation of the respective quinone derivative, 3,5-DTBQ which was purified by column chromatography. The product was isolated in high yield (71.1 %) by slow evaporation of the eluant and was identified by H^1 NMR spectroscopy (Fig. S2; Supporting Information). H^1 NMR ($CDCl_3$, 400 MHz): δ_H = 1.16 (s, 9H), 1.20 (s, 9H), 6.15 (d, J = 2.4 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H).

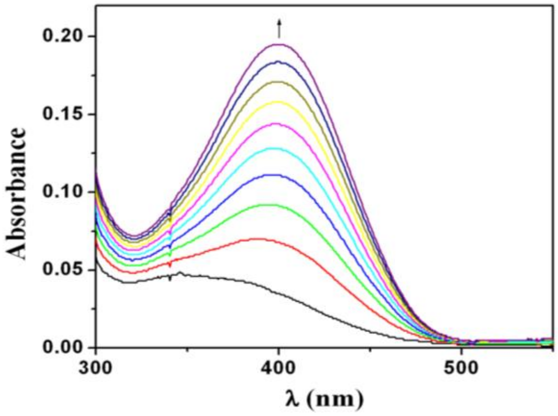


Fig. 2 Change in spectral pattern of complex **1** in DCM after reaction with 3,5-DTBC, observing the reaction for 4 h.

In order to find out the comparative reaction velocity between 3,5-DTBC and **1**, the reaction kinetics between **1** and 3,5-DTBC was studied by observing the time dependent change in absorbance at a wavelength of 401 nm, which is characteristic of 3,5-DTBQ in DCM. The colour of the solution gradually turned deep brown indicative of gradual conversion of 3,5-DTBC to 3,5-DTBQ. The difference in absorbance ΔA at 401 nm, was plotted against time to obtain the initial rate for that particular catalyst to substrate concentration ratio (Fig. 3). A first-order catalytic reaction is observed, with initial rate 6.2 × 10^{-3} min^{-1}. The reaction follows a pseudo first order kinetics in oxygen-saturated solvent medium.

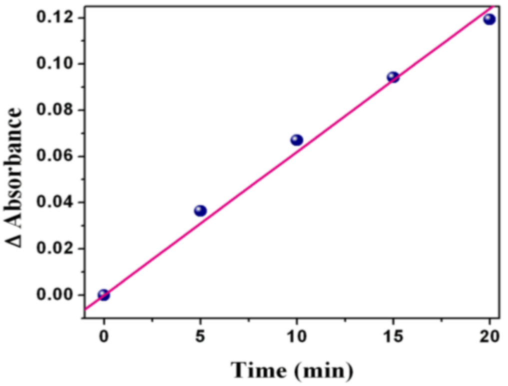


Fig. 3 A plot of the difference in absorbance (ΔA) vs time to evaluate the initial rate of the catalytic oxidation of 3,5-DTBC by **1** in DCM.

The catecholase activity of complex **1** was similarly studied in MeOH and MeCN media. In MeOH and MeCN also, 3,5-DTBQ shows maximum absorption at 401 nm (Fig. 4 and Fig. 5). 3,5-DTBQ obtained in each medium was purified by column chromatography with yields 67.8% in MeOH and 76.5% in MeCN. This was characterized by determining its melting point (~110°C) which agreed well with that reported in literature.[18] The reaction kinetics was studied by observing the time dependent change in absorbance at a wavelength of 401 nm for catalysis in MeOH as well as in MeCN. The difference in absorbance ΔA at this particular wavelength, were plotted against time to obtain the

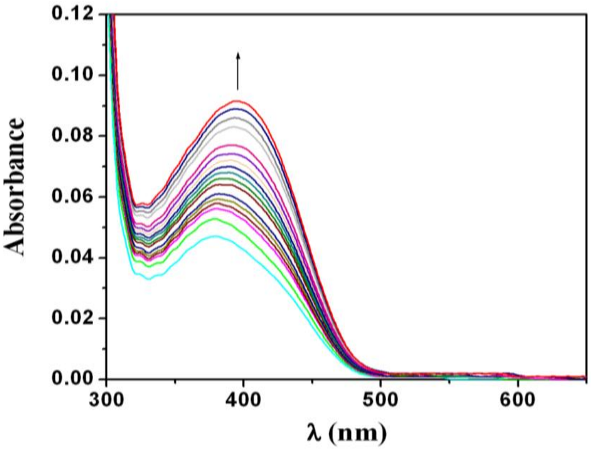


Fig. 4 Change in spectral pattern of complex **1** after reaction with 3,5-DTBC, observing the reaction for 6 h in MeOH.

initial rate of the reaction. A first-order catalytic reaction is observed in both the solvents, where the initial rates are found to be 8.98 × 10^{-4} min^{-1} and 1.09 × 10^{-3} min^{-1} respectively in MeOH and MeCN (Fig. S3 and Fig. S4; Supporting Information).

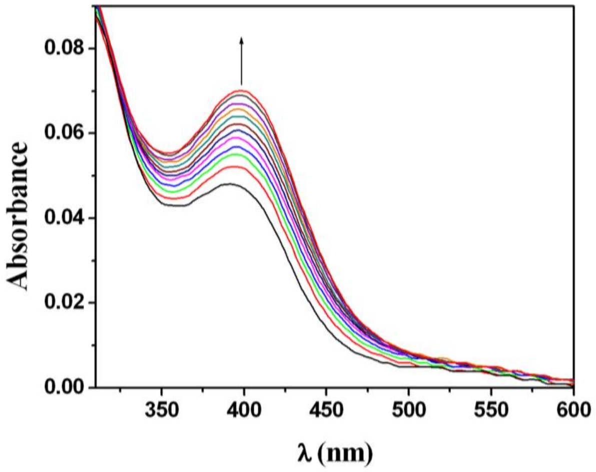


Fig. 5 Change in spectral pattern of complex **1** in MeCN after reaction with 3,5-DTBC, observing the reaction for 6 h.

Enzyme kinetics study

Enzymatic kinetic experiments were performed UV-Vis spectrophotometrically thermostated at 25°C with complex **1** and the substrate 3,5-DTBC in DCM, MeOH and MeCN. 0.04 ml of the complex solution, with a constant concentration of 1 × 10^{-4} M, was added to 2 ml of 3,5-DTBC of a particular concentration (varying its concentration from 1 × 10^{-3} M to 1 × 10^{-2} M) to achieve the ultimate concentration of the complex as 1 × 10^{-4} M. The conversion of 3,-5-DTBC to 3,5-DTBQ was monitored with time at a wavelength of 401 nm for solutions in DCM, MeOH and MeCN. The rate for each concentration of the substrate was determined by the initial rate method.

The rate versus concentration of substrate data were analyzed on the basis of Michaelis-Menten approach of enzymatic kinetics to get the Lineweaver-Burk (double reciprocal) plot as well as the values of the various kinetic parameters V_{max}, K_M and K_{cat}. The observed rate vs. [substrate] plot in DCM solution as well as Lineweaver-Burk plot is given in Fig. 6.

Similar plots in MeOH and MeCN are given in Fig. S5 and Fig. S6; Supporting Information. The kinetic parameters are listed in Table 3. The turnover numbers (K_{cat}) are 1.46 × 10^3, 1.21 × 10^3 and 2.16 × 10^3 h^{-1} in DCM, MeOH and MeCN, respectively.

Table 3 Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by **1**.

Solvent	V_{max} (M s^{-1})	Std. error	K_M (M)	Std. error	K_{cat} (h^{-1})
DCM	4.06 × 10^{-5}	5.71 × 10^{-6}	1.25 × 10^{-3}	2.29 × 10^{-4}	1.46 × 10^3
MeOH	3.36 × 10^{-5}	3.39 × 10^{-6}	7.38 × 10^{-4}	5.97 × 10^{-5}	1.21 × 10^3
MeCN	5.99 × 10^{-5}	1.98 × 10^{-5}	4.90 × 10^{-3}	2.36 × 10^{-3}	2.16 × 10^3

Reaction Mechanism

The catalytic process follows a two-step mechanistic pathway. This is evident from the rate plot (Fig. S7; Supporting information). The first step, with a lesser rate constant value, is the rate determining step. Probably, in this step, the 1:1 adduct of catechol and the cobalt complex is formed. In order to obtain a mechanistic inference of the catecholase activity and to get an idea about the complex-substrate intermediate, we recorded an ESI-MS spectrum (Fig. S8; Supporting information) of a 1:100 mixture of complex **1** and 3,5-DTBC of mixing them together. The signal at m/z = 196 is due to the formation of the protonated ligand $[(L_2)H]^+$. 3,5-DTBC can be indicated by the peak at m/z = 221. The peak at m/z = 243 can be assigned to sodium aggregate of quinone $[3,5\text{-DTBQ-Na}]^+$. The aqueous complex $[Co(L)_2(H_2O)]^+$ exhibits a peak at m/z = 463. Formation of a sodium aggregate of the species **1a** (Scheme 1) is identified by the peak at m/z = 354. The intermediate Co(III) complex is reduced to Co(II) by the catechol derivative and 3,5-DTBC itself gets oxidised to quinone in presence of oxygen. The oxygen that takes part in this process is converted to H_2O_2. H_2O_2 thus liberated was identified and characterized spectrophotometrically (S1; Supporting information).[19]

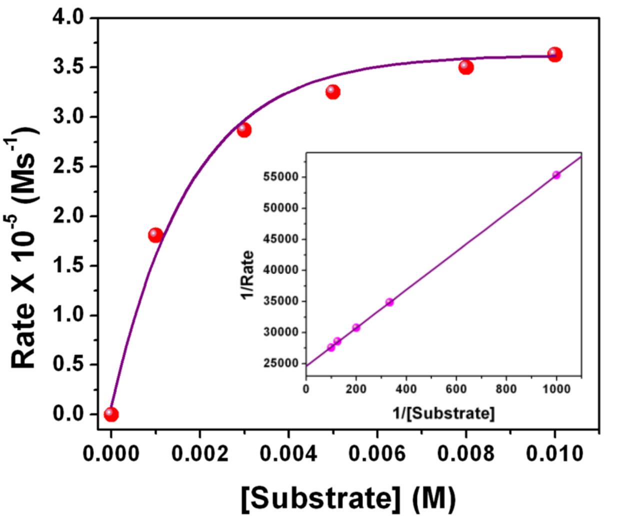
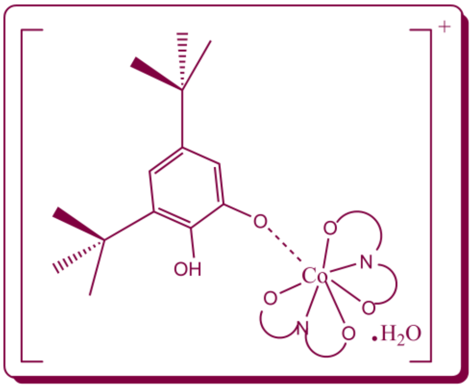


Fig. 6 Plot of rate vs. [substrate] in presence of **1** in DCM; inset: Lineweaver-Burk plot.



1a (Scheme 1)

Conclusions

In conclusion, we have synthesized and structurally characterized one monometallic cobalt(III) complex (**1**) with an (N,O) donor

Schiff base ligand. The catalytic property of **1** has been kinetically investigated for the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ in DCM, MeOH and MeCN which reveals that the catalytic reaction follows first order reaction pathway. The turnover numbers of **1** are 1.46×10^3, 1.21×10^3 and 2.16×10^3 h^{-1} in DCM, MeOH and MeCN, respectively which are much greater than those reported in recent times. In a recent report by Mohanta *et al*, the turnover numbers are 39 h^{-1}, 40 h^{-1}, and 48 h^{-1} in DMF, and 167 h^{-1} and 215 h^{-1} in MeCN for Cu(II) complexes.[4b] The same group reported a mixed valence Co(III/II) complex with turnover numbers 482.16 h^{-1} and 45.38 h^{-1} in MeCN and MeOH, respectively.[11] Rajak *et al* reported two Cu(II) complexes which show a turnover rate of about 29 and 37 h^{-1}.[4e] A turnover rate of 28 h^{-1} of a Cu(II) complex is reported by Neves *et al*.[5b] Ghosh *et al* reported three Ni(II) complexes with turnover numbers 64.1, 51.1 and 81.7 h^{-1} in MeCN,[8] and three heterometallic Ni(II)-Mn(II) complexes with their turnover rates ranging from 25.8 to 104.5 h^{-1}.[9] This indicates that **1** is a better and effective model for catecholase activity than the recent reported ones, though, to the best of our knowledge, the most active catalyst[4a] reported so far, exhibits a turnover number of 3.24×10^4 h^{-1}. So comparing all these data it can be concluded that the reported complex (**1**) is quite an efficient catalyst and has an appreciable turnover rates in various solvents. Besides, **1** being a mononuclear complex with non-copper centre is mimicking an enzyme with a dicopper active site.

Acknowledgement

Financial support by the Department of Science & Technology, New Delhi, India (F. No. SR/FT/CS-83/2010 dt. 11-02-2011) is gratefully acknowledged by RG. Generous help in magnetic data collection and mass spectrometric analysis respectively by Prof. T. Mallah, Université Paris Sud, France and Prof. M. Ali, Jadavpur University, India are also acknowledged. MM is thankful to The University of Burdwan for her research fellowship.

Notes and references

1 T. Klabunde, C. Eicken, J. C. Sacchettini and B. Krebs, *Nat. Struct. Biol.*, 1998, **5**, 1084.

2 (a) M. Merkel, N. Möller, M. Piacenza, S. Grimme, A. Rompel and B. Krebs, *Chem. Eur. J.*, 2005, **11**, 1201; (b) J. Reim and B. Krebs, *J. Chem. Soc., Dalton Trans*., 1997, 3793; (c) B. Sreenivasulu, F. Zhao, S. Gao and J. J. Vittal, *Eur. J. Inorg. Chem*., 2006, 2656; (d) C. -T. Yang, M. Vetrichelvan, M. Yang, B. Moubaraki, K. S. Murrey and J. J. Vittal, *Dalton Trans*., 2004, 113.

3 (a) I. A. Koval, P. Gamez, C. Belle, K. Selmeczi and J. Reedijk, *Chem. Soc. Rev*., 2006, **35**, 814; (b) I. A. Koval, K. Selmeczi, C. Belle, C. Philouze, E. Saint-Aman, I. Gautier-Luneau, A. M. Schuitema, M. van Vliet, P. Gamez, O. Roubeau, M. Lüken, B. Krebs, M. Lutz, A. L. Spek, J. -L. Pierre and J. Reedijk, *Chem. Eur. J.*, 2006, **12**, 6138.

4 (a) K. S. Banu, T. Chattopadhyay, A. Banerjee, S. Bhattacharya, E. Suresh, M. Nethaji, E. Zangrando and D. Das, *Inorg. Chem*., 2008, **47**, 7083; (b) S. Majumder, S. Sarkar, S. Sasmal, E. Carolina Sãnudo and S. S. Mohanta, *Inorg. Chem*., 2011, **50**, 7540; (c) A. Biswas, L. K. Das, M. G. B. Drew, C. Diaz and A. Ghosh, *Inorg. Chem*., 2012, **51**, 10111; (d) S. Mandal, J. Mukherjee, F. Lloret and R. Mukherjee, *Inorg. Chem*., 2012, **51**, 13148; (e) A. Banerjee, S. Sarkar, D. Chopra, E. Colacio and K. K. Rajak, *Inorg. Chem*., 2008, **47**, 4023.

5 (a) P. Comba, B. Martin, A. Muruganantham and J. Straub, *Inorg. Chem*., 2012, **51**, 9214; (b) A. Neves, L. M. Rossi, A. J. Bortoluzzi, B. Szpoganicz, C. Wiezbicki and E. Schwingel, *Inorg. Chem*., 2002, **41**, 1788; (c) S. Torelli, C. Belle, I. Gautier-Luneau, J. L. Pierre, E. Saint-Aman, J. M. Latour, L. L. Pape and D. Luneau, *Inorg. Chem*., 2000, **39**, 3526; (d) S. -C. Cheng and H. -H. Wei, *Inorg. Chim. Acta*, 2002, **340**, 105.

6 (a) A. L. Abuhijleh, J. Pollitte and C. Woods, *Inorg. Chim. Acta*, 1994, **215**, 131; (b) A. L. Abuhijleh, C. Woods, E. Bogas and G. L. Guenniou, *Inorg. Chim. Acta*, 1992, **195**, 67; (c) M. R. Malachowski, M. G. Davidson and J. N. Hoffman, *Inorg. Chim. Acta*, 1989, **157**, 91; (d) M. R. Malachowski and M. G. Davidson, *Inorg. Chim. Acta*, 1989, **162**, 199; (e) M. Mitra, A. K. Maji, B. K. Ghosh, G. Kaur, A. Roy Choudhury, C. -H. Lin, J. Ribas and R. Ghosh, *Polyhedron*, 2013, **61**, 15.

7 (a) P. Kar, R. Haldar, C. J. Gómez-García and A. Ghosh, *Inorg. Chem*., 2012, **51**, 4265; (b) S. Mukherjee, T. Weyhermüller, E. Bothe, K. Wieghardt and P. Chaudhuri, *Dalton Trans*., 2004, 3842; (c) K. S. Banu, T. Chattopadhyay, A. Banerjee, M. Mukherjee, S. Bhattacharya, G. K. Patra, E. Zangrando and D. Das, *Dalton Trans*., 2009, 8755.

8 A. Biswas, L. K. Das, M. G. B. Drew, G. Aromí, P. Gamez and A. Ghosh, *Inorg. Chem*., 2012, **51**, 7993.

9 P. Seth, L. K. Das, M. G. B. Drew and A. Ghosh, *Eur. J. Inorg. Chem*., 2012, 2232.

10 (a) L. I. Simándi, T. M. Simándi, Z. May and G. Besenyei, *Coord. Chem. Rev*., 2003, **245**, 85; (b) T. Megyes, Z. May, G. Schubert, T. Grósz, L. I. Simándi and T. Radnai, *Inorg. Chim. Acta*, 2006, **359**, 2329; (c) Z. May, L. I. Simándi and A. J. Vértes, *Mol. Cat*., 2007, **266**, 239; (d) S. -I. Lo, J. -W. Lu, W. -J. Chen, S. -R. Wang, H. -H. Wei and M. Katada, *Inorg. Chim. Acta*, 2009, **362**, 4699; (e) M. Mitra, A. K. Maji, B. K. Ghosh, P. Raghavaiah, J. Ribas and R. Ghosh, *Polyhedron*, 2014, **67**, 19.

11 S. Majumder, S. Mondal, P. Lemonie and S. S. Mohanta, *Dalton Trans*., 2013, **42**, 4561.

12 A. Guha, T. Chattopadhyay, N. D. Paul, M. Mukherjee, S. Goswami, T. K. Mondal, E. Zangrando and D. Das, *Inorg. Chem*., 2012, **51**, 8750.

13 S. Yamada, Y. Kuge and K. Yamanouchi, *Bull. Chem. Soc. Japan*, 1970, **43**, 406.

14 (a) S. Hazra, R. Koner, P. Lemoine, E. Carolina Sañudo and S. Mohanta, *Eur J. Inorg. Chem*., 2009, 3458; (b) R. Koner, S. Hazra, M. Fleck, A. Jana, C. R. Lucas and S. Mohanta, *Eur J. Inorg. Chem.*, 2009, 4982.

15 G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112.

16 L. J. Farrugia, 1998, ORTEP-32 for Windows. University of Glasgow, Scotland.

17 F. Zippel, F. Ahlers, R. Werner, W. Haase, H. -F. Nolting and B. Krebs, *Inorg. Chem*., 1996, **35**, 3409.

18 S. Tsuruya, S. -I. Yanai and M. Masai, *Inorg. Chem*., 1986, **25**, 141.

19 (a) A. I. Vogel, Textbook of quantitative inorganic analysis, 3rd ed., Longmans, Green and Co. Ltd., London, 1961, 366; (b) A. Neves, L. M. Rossi, A. J. Bortoluzzi, B. Szpoganicz, C. Wiezbicki and E. Schwingel, *Inorg. Chem*., 2002, **41**, 1788; (c) E. Monzani, L. Quinti, A. Perotti, L. Casella, M. Gullotti, L. Randaccio, S. Geremia, G. Nardin, P. Faleschini and G. Tabbi, *Inorg.Chem.*, 1998, **37**, 553.