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Synthesis, crystal structure and catecholase activity of [Co(SCN)₂(L)] [L = N,N'-(bis(pyridine-2-yl)benzilidene)-1,2-ethanediamine]

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Crystallographically characterized $[Co(SCN)_2(L)]$ [L = N,N'-(bis(pyridine-2-yl)benzilidene)-1,2-ethanediamine] (1) as the functional model of catecholase activity was synthesized and characterized. The catechol-quinone conversion in presence f aerial oxygen and 1 was found in methanol and acetonitrile. In each case Michaelis-Menten kinetics were followed to prove the biomimicking nature of 1.



Synthesis, crystal structure and catecholase activity of $[Co(SCN)_2(L)]$ [L = N,N'-(bis(pyridine-2-yl)benzilidene)-1,2-ethanediamine]

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Abstract

Synthesis and structural characterization of a mononuclear cobalt(II) complex $[Co(SCN)_2(L)]$ [L = N,N'-(bis(pyridine-2-yl)benzilidene)-1,2-ethanediamine] (1) is reported. Molecular geometry of the complex is found to be distorted octahedron with CoN_4S_2 chromophore. 1 is shown to respond in catecholase activity in methanol and acetonitrile. In each solvent Michaelis-Menten reaction kinetics were followed. The reaction mechanism of the catecholase activity is investigated using mass spectrometry.

Key words: Cobalt, Schiff base, X-ray structure, catecholase activity

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1. Introduction

The active site structure of the plant enzyme catecholase which catalyzes oxidation of catechol to quinone in presence of molecular oxygen appeared in 1998 [1]. Antiferromagnetically coupled dinuclear Cu(II) in the active site of the enzyme encouraged the researchers round the globe since then to model small dinuclear Cu(II) complexes to mimic the

enzyme and its activity [2-5]. In addition to this some mononuclear Cu(II) complexes [6] and complexes of some transition metals other than Cu(II) like manganese [6e, 7], nickel [8], iron [9], cobalt [10], zinc [11], vanadium [12], etc also appeared in literature. Schiff bases are important and popular class of ligands because of their preparational accessibilities, varied structural motifs, etc. Chemistry of Cobalt-Schiff base complexes have attracted much attention in the field of coordination chemistry as they exhibit different structural features and varied applications covering catalysis, photochemistry, electrochemistry and biological inorganic chemistry [13-15]. In continuation to our interest in synthesizing a number of non-copper transition metal complexes particularly the mononuclear cobalt complex here we present synthesis and X-ray structural characterization of a mononuclear cobalt(II) complex with neutral (N,N) donor ligand $[Co(SCN)_2(L)]$ [L = N,N'-(bis(pyridine-2-yl)benzilidene)-1,2-ethanediamine,Scheme 1] (1) which did show catalyzing the aerial oxidation of 3,5-ditertiary butyl catechol to corresponding quinone. The catalytic results are found in methanol and acetonitrile solvents and in each case reaction rates and turn over numbers were measured. The measurement Michelis-Menten kinetics in each solvent supported the biomimicking nature of the synthesized compound.



Scheme 1: (N^p,Nⁱ,Nⁱ, N^p) donor set in L

2. Experimental

2.1.Materials

High purity 2-benzoylpyridine (Sigma Aldrich, India), ethylenediamine (Sigma Aldrich, India), ammonium thiocyanate (E. Merck India), cobalt(II) perchlorate hexahydrate (Sigma Aldrich, India), 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.

Caution! Perchlorate compounds are potentially explosive [16] especially in the presence of organic ligands. Only a small amount of these materials should be prepared and handled with care.

2.2. X-ray diffraction

Single crystals of **1** for X-ray crystallographic analysis were selected following examination under a microscope. Diffraction data at 296 K were collected on a Bruker SMART APEX II CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal data and refinement details are listed in Table 1. **1** was identified as C 2/c space group. 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 0.318 and -0.254 eÅ⁻³ with no chemical significance. All calculations were carried out using SHELXL-97 [17] and were refined using SHELSL-97 [17] available within Olex-2 [18] suite. All the figures have been generated using ORTEP-32 [19].

2.3. 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 ¹HNMR spectral data of the quinine were collected in CDCl₃ on a Bruker 400 MHz spectrometer.

2.4. Synthesis of L

To a solution of 2-benzoylpyridine (0.499 g, 2.73 mmol) in 100 mL methanol, ethane-1,2-diamine (0.816 g, 1.36 mmol) was added. The mixture was refluxed for a period of 7-8 hours until a light yellow color developed. The resultant solution was partially dried in a water bath until a sticky yellow mass was obtained. Yield: 0.273 g (70%). *Anal.* calc. for $C_{26}H_{22}N_4$ (L): C, 79.97; H, 5.68; N, 14.35; Found: C, 79.70; H, 5.60; N, 14.28. Selected IR bands (KBr pellet, cm⁻¹): v(C=N) 1616. UV-Vis (λ , nm, MeOH): 254.

2.5. Synthesis of 1

The solution mixture resulted from the gradual addition of $Co(ClO_4)_2.6H_2O$ (0.0370 g; 0.1 mmol) to a methanolic solution of L (0.039g, 0.1 mmol) followed by addition of NH₄NCS in methanol (0.0152 g, 0.2 mmol) was stirred for 5 hours. The final solution mixture was filtered and kept undisturbed at room temperature. After 7 days, dark blue X-ray quality single crystals were obtained which were filtered off through a fine glass frit, washed with toluene and dried in a vacuum dessicator. Yield (on the basis of metal salt): 0.0267g (73%). Found C, 59.60; H, 4.00; N,15.00. Anal. Calc. for $C_{28}H_{22}N_6S_2Co: C$, 59.46; H, 3.92; N, 14.86. IR (KBr, Cm⁻¹): v(C=N) 1596; v(NCS) 2110. UV-Vis (CH₃CN, λ , nm): 496, 264.

3. Results and discussion

3.1. Synthesis and formulation

The Schiff base, N,N'-(bis(pyridine-2-yl)benzylidine)-1,2-ethanediamine (L) belonging to symmetrical N^p,Nⁱ,Nⁱ,N^p type backbone [N^p = N(pyridine) and Nⁱ = N(imine)], was prepared by condensation of 1:2 molar ratio of ethane-1,2-diamine and 2-benzoylpyridine in dehydrated ethanol. The hexacoordinated mononuclear complex **1** was isolated as dark blue crystalline product through one-pot synthesis of 1:1:2 molar ratio of Co(ClO₄)₂.6H₂O, L and NH₄NCS in methanol solution at room temperature. The compound is stable over long periods of time in powder or crystalline form and are soluble in common organic solvents such as methanol and acetonitrile but are insoluble in water. In IR, v(C=N) in the ligand appears at 1616 cm⁻¹ (Fig. S1(a); Supporting information) whereas the stretching frequency of the imine in the compound appears at 1596 cm⁻¹ (Fig. S1(b); Supporting information) [20]. Peak at 2110 cm⁻¹ represents the thiocyanato group in the compound (Fig. S1(b); Supporting information) [20]. The electronic spectrum of the complex in methanol solution exhibits a distinct strong and broad absorption bands at ~500 nm due to the ⁴T_{1g}(P) \rightarrow ⁴T_{1g}(P) transition, which is characteristic of distorted octahedral cobalt(II) center [21]. The bands at ~264 nm may be assigned to a ligand based transition [22].

3.2. X-ray structure

In order to define the coordination sphere conclusively, single-crystal X-ray diffraction study in **1** was made. The molecular view of the complex is shown in Fig. 1. Selected bond lengths and angles pertaining to the coordination sphere are set out in Table 2. The coordination polyhedron around cobalt(II) is best described as distorted octahedron with CoN_4S_2 chromophore. Two imine N atoms (N1 and N1*) and two pyridine N atoms (N2 and N2*) of L occupy the equatorial sites while two terminal S atoms (S1 and S1*) of two thiocyanates in mutual *trans* orientation [S1-Co- S1*: 175.13(4)°] are housed at the axial positions. The Co-N bond distances in the basal plane span the range 1.962(3)-1.866(2) Å and the difference Δ between the longest and shortest bond amounts 0.096 Å. Each of the axial bond is 2.3009(7) Å long.

In solid-state, the molecular units are packed through weak C-H...N hydrogen bond (Table 3) involving C8-H8A of the aromatic ring and N3ⁱ of thiocyanate (Fig. 2).

3.3. 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 methanol. 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 MeOH and MeCN (Figs. 3 and 4). Spectral bands at 264 and 496 nm appear in the electronic spectrum of complex **1**, whereas 3,5-DTBC shows a single band at 282 nm.

After addition of 3,5-DTBC, the time dependent spectral scan shows very smooth growing of quinone band at 400 nm, as reported by Krebs et al [23], indicates the formation of the respective quinone derivative, 3,5-DTBQ which was purified by column chromatography. The product obtained from each solvent was isolated in high yield (65% and 70%) by slow evaporation of the eluant and was identified by measuring melting point (~110°C) [24].

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 400 nm, which is characteristic of 3,5-DTBQ in solution. The colour of the solution gradually turns deep brown both in methanol and acetonitrile indicative of gradual conversion of 3,5-DTBC to 3,5-DTBQ. The difference in absorbance ΔA at 400 nm was plotted against time to obtain the velocity for that particular catalyst to substrate concentration ratio (Figs. 5 and 6). A first-order catalytic reaction is observed, with velocity $6.35 \times 10^{-4} \text{ min}^{-1}$ (MeOH) and 5.09×10^{-4} (MeCN).

3.4. Engyme kinetics study

Enzymatic kinetic experiments were performed UV-Vis spectrophotometrically thermostated at 25°C with complex **1** and the substrate 3,5-DTBC in MeOH. 0.05 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 400 nm for solution in MeOH. 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 methanol and acetonitrile solutions as well as Lineweaver-Burk plots are given in Fig. 7 and Fig. 8, respectively. The kinetic parameters are listed in Table 4. The turnover numbers (K_{cat}) are found to be 4.15×10^4 h⁻¹ and 3.06×10^5 h⁻¹ in MeOH and MeCN, repectively.

3.5. Mechanism of catecholase activity

The catalytic process follows a two-step mechanistic pathway. The first step is the rate determining step. Probably, in this step, the 1:1 adduct of catechol and the cobalt complex is formed. 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 of a 1:100 mixture of **1** and 3,5-DTBC (Figs. S2(a)-S2(d); Supporting information). The signal at m/z = 390.83 (Fig. S2(a); Supporting information) is due to the formation of the ligand N,N'-(bis(pyridine-2-yl)benzilidene)-1,2-ethanediamine. The metal complex **1** exhibits a peak at m/z = 565.49 (Fig. S2(b); Supporting information). The peak at m/z = 243.31 can be assigned to sodium aggregate of quinone [3,5-DTBQ]-Na⁺ (Fig. S2(c); Supporting information). The formation of a complex-substrate adduct intermediate species is identified by the peak at m/z = 669.77 (Fig. S2(d), Scheme S1; Supporting information). The catechol derivative, 3,5-DTBC to 3,5-DTBQ in this process is converted to H₂O₂. H₂O₂ thus liberated was identified and characterized spectrophotometrically (S1; Supporting information) [24].

4. Conclusion

Synthesis and X-ray structural characterization of a mononuclear cobalt-Schiff base complex **1** is reported. The compound shows catecholase activity in methanol and acetonitrile with high turn over numbers. Catecholase active cobalt complexes are rare [10]. Interestingly, the turn over number of the reported complex is better than the few reported ones [10]. Mechanistic investigation revealed that the substrate-product conversion in this case is occurred through a substrate-catalyst adduct. This is trapped my mass spectrometry.

5. Supplementary data

CCDC 1524439 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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References

- [1] T. Klabunde, C. Eicken, J. C. Sacchettini, B. Krebs, Nat. Struct. Biol. 5 (1998) 1084.
- [2] (a) M. Merkel, N. Möller, M. Piacenza, S. Grimme, A. Rompel, B. Krebs, Chem. Eur. J. 11 (2005) 1201; (b) J. Reim, B. Krebs, J. Chem. Soc. Dalton Trans. (1997) 3793; (c) B. Sreenivasulu, F. Zhao, S. Gao, J. J. Vittal, Eur. J. Inorg. Chem. (2006) 2656; (d) C. -T. Yang, M. Vetrichelvan, M. Yang, B. Moubaraki, K. S. Murrey, J. J. Vittal, Dalton Trans. (2004) 113.
- [3] (a) I. A. Koval, P. Gamez, C. Belle, K. Selmeczi, J. Reedijk, Chem. Soc. Rev. 35 (2006)
 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, J. Reedijk, Chem. Eur. J. 12 (2006) 6138.

- [4] (a) S. Dasgupta, I. Majumder, P. Chakraborty, E. Zangrando, A. Bauza, A. Frontera, D. Das, Eur. J. Inorg. Chem. In press, Doi: 10.1002/ejic.201600985; (b) S. Majumder, S. Sarkar, S. Sasmal, E. Carolina Sãnudo, S. S. Mohanta, Inorg. Chem. 50 (2011) 7540; (c) A. Biswas, L. K. Das, M. G. B. Drew, C. Diaz, A. Ghosh, Inorg. Chem. 51 (2012) 10111; (d) S. Mandal, J. Mukherjee, F. Lloret, R. Mukherjee, Inorg. Chem. 51 (2012) 13148; (e) A. Banerjee, S. Sarkar, D. Chopra, E. Colacio, K. K. Rajak, Inorg. Chem. 47 (2008) 4023.
- [5] (a) P. Comba, B. Martin, A. Muruganantham, J. Straub, Inorg. Chem. 51 (2012) 9214;
 (b) A. Neves, L. M. Rossi, A. J. Bortoluzzi, B. Szpoganicz, C. Wiezbicki, E. Schwingel, Inorg. Chem. 41 (2002) 1788; (c) S. Torelli, C. Belle, I. Gautier-Luneau, J. L. Pierre, E. Saint-Aman, J. M. Latour, L. L. Pape, D. Luneau, Inorg. Chem. 39 (2000) 3526; (d) J.A.F. de Oliveira, M.P. da Silva, B. de Souza, T.P. Camargo, B. Szpoganicz, A. Neves, A.J. Bortoluzzi, Dalton Trans. 45 (2016) 15294.
- [6] (a) A. L. Abuhijleh, J. Pollitte, C. Woods, Inorg. Chim. Acta 215 (1994) 131; (b) A. L. Abuhijleh, C. Woods, E. Bogas, G. L. Guenniou, Inorg. Chim. Acta 195 (1992) 67; (c) M. R. Malachowski, M. G. Davidson, J. N. Hoffman, Inorg. Chim. Acta 157 (1989) 91; (d) M. R. Malachowski, M. G. Davidson, Inorg. Chim. Acta 162 (1989) 199; (e) M. Mitra, A. K. Maji, B. K. Ghosh, G. Kaur, A. R. Choudhury, C.-H. Lin, J. Ribas, R. Ghosh, Polyhedron 61 (2013) 15.
- [7] (a) M. Maiti, D. Sadhukhan, S. Thakurta, E. Zangrando, G. Pilet, A. Bauźa, A. Frontera,
 B. Dede, S. Mitra, Polyhedron 75 (2014) 40; (b) A. Guha, K. S. Banu, A. Banerjee, T.
 Ghosh, S. Bhattacharya, E. Zangrando, D. Das, J. Mol. Cat. A: Chem. 338 (2011) 51;
 (c) P. Kar, Y. Ida, T. Kanetomo, M. G. B. Drew, T. Ishida, A. Ghosh, Dalton Trans. 44

(2015) 9795; (d) P. Chakraborty, I. Majumder, K. S. Banu, B. Ghosh, H. Kara, E. Zangrando, D. Das, Dalton Trans. 45 (2016) 742; (e) S. Mukherjee, T. Weyhermüller, E. Bothe, K. Wieghardt, P. Chaudhuri, Dalton Trans. (2004) 3842; (f) P. Chakraborty, S. Majumder, A. Jana, S. Mohanta, Inorg. Chim. Acta 410 (2014) 65.

- [8] (a) A. Guha, K. S. Banu, S. Das, T. Chattopadhyay, R. Sanyal, E. Zangrando, D. Das, Polyhedron 52 (2013) 669; (b) J. Adhikary, P. Chakraborty, S. Das, T. Chattopadhyay, A. Bauźa, S. K. Chattopadhyay, B. Ghosh, F. A. Mautner, A. Frontera, D. Das, Inorg. Chem. 52 (2013) 13442; (c) P. K. Basu, M. Mitra, A. Ghosh, L. Thander, C. -H. Lin, R. Ghosh, J. Chem. Sci. 126 (2014) 1635; (d) M. Das, R. Nasani, M. Saha, S. M. Mobin, S. Mukhopadhyay, Dalton Trans. 44 (2015) 2299.
- [9] (a) R. Singh, A. Banerjee, K. K. Rajak, Inorg. Chim. Acta 363 (2010) 3131; (b) M. Mitra, A. K. Maji, B. K. Ghosh, P. Raghavaiah, J. Ribas, R. Ghosh, Polyhedron 67 (2014) 19.
- [10] (a) S. Majumder, S. Mondal, P. Lemonie, S. Mohanta, Dalton Trans. 42 (2013) 4561;
 (b) M. Mitra, P. Raghavaiah, R. Ghosh, New J. Chem. 39 (2015) 200; (c) T.S. Mahapatra, D. Basak, S. Chand, J. Lengyel, M. Shatruk, V. Bertolasi, D. Ray, Dalton Trans. 45 (2016) 13576.
- [11] (a) A. Guha, T. Chattopadhyay, N. D. Paul, M. Mukherjee, S. Goswami, T. K. Mondal,
 E. Zangrando, D. Das, Inorg. Chem. 51 (2012) 8750; (b) S. K. Mal, M. Mitra, C. S.
 Purohit, R. Ghosh, Polyhedron 101 (2015) 191.
- [12] (a) B. Barua, A. Chakravorty, Indian J. Chem., 42A (2003) 2677; (b) B. Baruah, S. Das,
 A. Chakravorty, Inorg. Chem. 41 (2002) 4502; (c) S. P. Rath, K. K. Rajak, A. Chakravorty, Inorg. Chem. 38 (1999) 4376; (d) C. Mukherjee, T. Weyhermüller, E.

Bothe, P. Chaudhuri, Inorg. Chem. 47 (2008) 11620; (e) S. K. Mal, M. Mitra, H. R. Yadav, C. S. Purohit, A. R. Choudhury, R. Ghosh, Polyhedron 111 (2016) 118.

- [13] (a) S. Shit, D. Saha, D. Saha, T.N.G. Row, C. Rizzoli, Inorg. Chim. Acta, 415 (2014) 103; (b) Y.N. Belokon, V.I. Maleev, M. North, V.A. Larionov, T F. Savel'Yeva, A. Nijland, Y.V. Nelyubina, ACS Catalysis 3 (2013) 1951; (c) E. Vinck, E. Carter, D.M. Murphy, D.S. Van, Inorg. Chem. 51 (2012) 8014.
- [14] (a) M. Volpe, H. Hartnett, J.W. Leeland, K. Wills, M. Ogunshun, B.J. Duncombe, C. Wilson, J.B. Love, Inorg. Chem., 48 (2009) 5195; (b) T. Honda, T. Kojima, S. Fukuzumi, J. Am. Chem. Soc., 134 (2012) 4196; (c) A. Kamath, N.V. Kulkarni, P.P. Netalkar, V.K. Revankar, *Spectrochim Acta Part A*, 79 (2011) 1418.
- [15] (a) P.K. Mascharak, Coord. Chem. Rev., 225 (2002) 201; (b) M. Salehi, M. Amirnasr,
 S. Meghdadi, K. Mereiter, H.R. Bijanzadeh, A. Khaleghian, Polyhedron 81 (2014) 90;
 (c) K. Bhar, S. Khan, J. S. Kosta, J. Ribas, O. Roubeau, P. Mitra, B. K. Ghosh, Angew
 Chem. Int. Ed. 124 (2012) 2184.
- [16] W. C. Wolsey, J Chem Educ, 50 (1973) A335.
- [17] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
- [18] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339.
- [19] L.J. Farrugia, 1998, ORTEP-32 for Windows. University of Glasgow, Scotland.
- [20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry (John Wiley & Sons Inc, New York), 1997.
- [21] R. Kapoor, A. Pathak, P. Kapoor, P. Venugopalan, Polyhedron 25 (2006) 31.

- [22] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, New York, 1984.
- [23] F. Zippel, F. Ahlers, R. Werner, W. Haase, H.-F. Nolting, B. Krebs, Inorg. Chem. 35 (1996) 3409.
- [24] (a) S. Tsuruya, S.-I. Yanai and M. Masai, Inorg. Chem. 25 (1986) 141; (b) M. Mitra, T. Kundu, G. Kaur, G. Sharma, A.R. Choudhury, Y. Singh, R. Ghosh, RSC Adv. 6 (2016) 58831.
- [25] (a) A. I. Vogel, *Textbook of quantitative inorganic analysis*, (Ed.: 3rd) Longmans, Green and Co. Ltd., London, 1961, pp-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.

Empirical formula	$C_{28}H_{22}N_6S_2Co$
Formula weight	565.59
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 12.3213(2) Å, b = 12.7748(2) Å, c = 18.6805(3) Å
	$\alpha = 90^{\circ}, \ \beta = 99.2270(10)^{\circ}, \ \gamma = 90^{\circ}$

Table 1. Crystal data and structure refinement parameter for 1

Volume	2902.30(8) Å ³		
Ζ	8		
Density (calculated)	1.294 Mg/m ³		
Absorption coefficient	0.762 mm ⁻¹		
F(000)	1164		
Crystal size	$0.18 \times 0.10 \times 0.08 \ mm^3$		
Theta range for data collection	2.21 to 28.31°		
Index ranges	-16<=h<=16, -17<=k<=14, -24<=l<=24		
Reflections collected	14405		
Independent reflections	3605 [R(int) = 0.0512]		
Completeness to theta = 28.31°	99.9 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9416 and 0.8751		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	3605/0/168		
Goodness-of-fit on F ²	0.933		
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.0970		
Largest diff. peak and hole	0.318 and -0.254 eÅ ⁻³		

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

Bond distances

Co(1)-N(1)	1.866(2)	Co(1)-N(2)	1.963(2)
Co(1)-N(1)*	1.866(2)	Co(1)-S(1)*	2.3009(7)
Co(1)-N(2)*	1.963(2)	Co(1)-S(1)	2.3009(7)
Bond angles			
N(1)-Co(1)-N(1)*	86.42(13)	N(1)*-Co(1)-S(1)	92.26(7)
N(1)-Co(1)-N(2)*	81.77(9)	N(2)*-Co(1)-S(1)	82.96(6)
N(1)*-Co(1)-N(2)*	167.14(9)	N(2)-Co(1)-S(1)	94.25(6)
N(1)-Co(1)-N(2)	167.14(9)	S(1)*-Co(1)-S(1)	175.13(4)
N(1)*-Co(1)-N(2)	81.77(9)	N(1)*-Co(1)-S(1)*	91.29(7)
N(2)*-Co(1)-N(2)	110.42(13)	N(2)*-Co(1)-S(1)*	94.25(6)
N(1)-Co(1)-S(1)*	82.96(6)	N(2)-Co(1)-S(1)*	82.96(6)
N(1)-Co(1)-S(1)	91.29(7)		

 Table 3. Hydrogen bonding interaction parameters

Hydrogen bond parameters (Å, °)					
D-H···A	D-H	Н…А	D····A	D-H···A	
C8-H8A···N3 ⁱ	0.9300	2.5100	3.274(5)	140.00	

Table 4. Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by $\mathbf{1}$

Compd	Solvent	V_{max} (M s ⁻¹)	Std. error	$K_M(M)$	Std. error	K_{cat} (h ⁻¹)

1	MeOH	1.29×10 ⁻⁵	2.62×10^{-6}	1.15×10^{-3}	3.94×10^{-4}	4.15×10^{4}
1	MeCN	4.99× 10 ⁻⁴	7.52×10^{-5}	8.50×10^{-3}	1.76×10^{-3}	3.06×10^{5}



Fig. 1 Molecular view of 1 with 20% ellipsoid probability



Fig. 2. 2D sheet structure in 1 through C-H...N hydrogen bonding





Fig. 3. Change in spectral pattern of reaction of 1 with 3,5-DTBC in MeOH after

Fig. 4. Change in spectral pattern of reaction of 1 with 3,5-DTBC in MeCN after

observing the reaction for 6 h





Fig. 5. A plot of the difference in absorbance (ΔA) vs time to evaluate the initial velocity of the

catalytic oxidation of 3,5-DTBC by 1 in MeOH

Fig. 6. A plot of the difference in absorbance (ΔA) vs time to evaluate the initial velocity

of the catalytic oxidation of 3,5-DTBC by 1 in MeCN



Fig. 7. Plot of rate vs. [substrate] in the presence of 1 in MeOH; inset: Lineweaver-Burk plot



Fig. 8. Plot of rate vs. [substrate] in the presence of 1 in MeCN; inset: Lineweaver-Burk plot

- Cobalt chemistry
- Schiff base
- Bioinspired catalysis
- Catecholase activity