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## Correction: Mixed azido/phenoxido bridged trinuclear Cu(II) complexes of Mannich bases: Synthesis, structures, magnetic properties and catalytic oxidase activities

Avijit Das,<sup>a</sup> Kisholoy Bhattacharya,<sup>a,b</sup> Lakshmi Kanta Das,<sup>c</sup> Sanjib Giri<sup>a,d</sup> and Ashutosh Ghosh<sup>\*a</sup>DOI: 10.1039/d0dt90032j  
rsc.li/daltonCorrection for 'Mixed azido/phenoxido bridged trinuclear Cu(II) complexes of Mannich bases: Synthesis, structures, magnetic properties and catalytic oxidase activities' by A. Ghosh *et al.*, *Dalton Trans.*, 2018, **47**, 9385–9399.

In response to the overestimation of  $k_{\text{cat}}$  values for the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) and *o*-aminophenol (OAP) catalysed by the complexes reported in the paper (*Dalton Trans.*, 2018, **47**, 9385–9399) that has been pointed out by Laura Gasque *et al.*,<sup>1</sup> we regret that there are some mistakes and these have been corrected below. These corrections do not affect the discussion or conclusions of the original article.

(1) We analyzed the kinetic data for oxidation of 3,5-DTBC to 3,5-DTBQ by the “integrated rate method” not by the “initial rate method”. Therefore, the sentence on page 9392, right column, last paragraph should be changed to “The kinetics of oxidation of 3,5-DTBC to 3,5-DTBQ by 1–3 were determined by the integrated rate method by monitoring the growth of the quinone band at 402 nm as a function of time”.

(2) To avoid any confusion for readers, the caption of Fig. 6 should be changed to “Increase of the 3,5-DTBQ band at around 401 nm after mixing of equal volumes of 3,5-DTBC ( $1 \times 10^{-2}$  M) and a methanolic solution of complex 2 ( $1 \times 10^{-4}$  M). The spectra were recorded at 5 min intervals for 60 min”.

(3) The calc. rate/“rate” factors calculated by Laura Gasque *et al.*<sup>1</sup> for these complexes are incorrect, as the concentration of the catalyst and the concentration of the substrate are halved after mixing. This factor also depends upon the concentration of substrate. We have recalculated the calc. rate/“rate” factors for complexes 1–3 with the correct concentrations of catalyst and with

**Table 1** Spectral and kinetic parameters of complexes for [S] : [cat] = 100 : 1 and 10 : 1 for the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to 3,5-di-*tert*-butylquinone (3,5-DTBQ) and comparison of the calc. rate with the rate

| Complex | [S] (M) <sup>a</sup> | [Cat] (M) <sup>a</sup> | $\Delta$ Absorbance for 5 min <sup>d</sup> | Rate <sup>b</sup> (M min <sup>-1</sup> ) | $V_M$ (M min <sup>-1</sup> ) | $k_{\text{cat}}$ (h <sup>-1</sup> ) | $K_M$ (M)              | Calc. rate ( $V_0$ ) <sup>c</sup> | $V_0/\text{rate}$ |
|---------|----------------------|------------------------|--|--|------------------------------|-------------------------------------|------------------------|-----------------------------------|-------------------|
| 1       | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.41                                       | $5.03 \times 10^{-5}$                    | $4.74 \times 10^{-4}$        | 568.8                               | $46.63 \times 10^{-4}$ | $24.53 \times 10^{-5}$            | 4.8               |
|         | $5 \times 10^{-4}$   | $5 \times 10^{-5}$     | 0.28                                       | $3.44 \times 10^{-5}$                    | $4.74 \times 10^{-4}$        | 568.8                               | $46.63 \times 10^{-4}$ | $4.59 \times 10^{-5}$             | 1.2               |
| 2       | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.37                                       | $4.54 \times 10^{-5}$                    | $4.52 \times 10^{-4}$        | 542.1                               | $47.96 \times 10^{-4}$ | $23.04 \times 10^{-5}$            | 5.2               |
|         | $5 \times 10^{-4}$   | $5 \times 10^{-5}$     | 0.25                                       | $2.57 \times 10^{-5}$                    | $4.52 \times 10^{-4}$        | 542.1                               | $47.96 \times 10^{-4}$ | $4.26 \times 10^{-5}$             | 1.3               |
| 3       | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.33                                       | $4.05 \times 10^{-5}$                    | $4.17 \times 10^{-4}$        | 500.4                               | $50.43 \times 10^{-4}$ | $20.76 \times 10^{-5}$            | 5.1               |
|         | $5 \times 10^{-4}$   | $5 \times 10^{-5}$     | 0.21                                       | $2.58 \times 10^{-5}$                    | $4.17 \times 10^{-4}$        | 500.4                               | $50.43 \times 10^{-4}$ | $3.76 \times 10^{-5}$             | 1.5               |

<sup>a</sup>The effective concentrations of complex and substrate after mixing are halved with respect to their initial concentrations because both are mixed with equal volumes. <sup>b</sup>Rate has been calculated using  $1630 \text{ M}^{-1} \text{ cm}^{-1}$  as the molar absorptivity of the product. <sup>c</sup>Calculated rate has been determined using the equation:  $V_0 = \frac{V_M[S]}{[S] + K_M}$ . <sup>d</sup> $\Delta$ Absorbance for time gaps of 5 min has been measured from 90 s to 390 s.

<sup>a</sup>Department of Chemistry, University College of Science, University of Calcutta, 92, A. P.C. Road, Kolkata 700009, India. E-mail: ghosh\_59@yahoo.com

<sup>b</sup>Department of Chemistry, Adamas University, Barasat-Barrackpore Road, Barasat 700126, West Bengal, India

<sup>c</sup>Department of Chemistry, Government General Degree College at Kharagpur-II, Ambigeria, Madpur, Paschim Medinipur, 721149 West Bengal, India



different concentrations of substrate (Table 1). From these calculations, one can see that the calc. rate/"rate" factors do not exceed  $\sim 5$  for any of these compounds. They are close to  $\sim 1$  for lower concentrations of substrate as expected.

(4) The kinetic parameters for the oxidation of *o*-aminophenol in the original paper were calculated by the "integrated rate method". We agree that calculation of  $k_{\text{cat}}$  for oxidation of *o*-aminophenol by the "integrated rate method" is a mistake considering the high  $\epsilon$  value of APX. Moreover, we noticed that after about 2 hours of time the absorbance apparently becomes constant, and we used that incorrectly as  $A_{\infty}$ , but the constant absorbance is probably due to polymerization or formation of other compounds. Hence, in the original report, the catalytic activities were grossly overestimated and we obtained incongruous  $k_{\text{cat}}$  values.

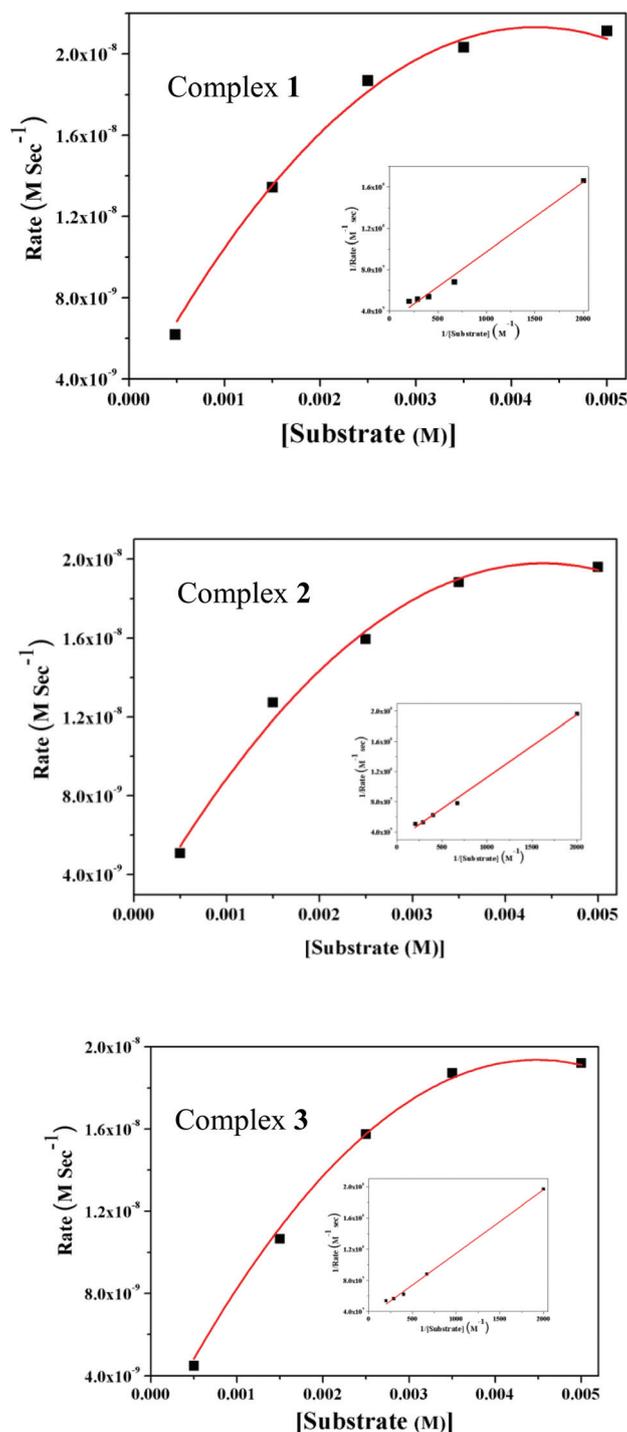


Fig. 1 Plots of rate vs. substrate concentration for complexes 1–3. Insets show the corresponding Lineweaver–Burk plots.



**Table 2** Kinetic parameters for the oxidation of *o*-aminophenol catalyzed by complexes 1–3

| Complexes | [Cat] (M)          | $V_{\max}$ (M s <sup>-1</sup> ) | $K_M$ (M)             | $k_{\text{cat}}$ (h <sup>-1</sup> ) |
|-----------|--------------------|---------------------------------|-----------------------|-------------------------------------|
| 1         | $5 \times 10^{-5}$ | $3.45 \times 10^{-8}$           | $2.32 \times 10^{-3}$ | 2.5                                 |
| 2         | $5 \times 10^{-5}$ | $3.37 \times 10^{-8}$           | $2.80 \times 10^{-3}$ | 2.4                                 |
| 3         | $5 \times 10^{-5}$ | $3.05 \times 10^{-8}$           | $2.46 \times 10^{-3}$ | 2.2                                 |

**Table 3** Spectral and kinetic parameters of complexes for the oxidation of *o*-aminophenol (OAP) and comparison of the calc. rate with the experimental rate

| Complex   | [S] <sup>a</sup> (M) | [Cat] <sup>a</sup> (M) | $\Delta$ Absorbance for 5 min (0–5 min) | Rate <sup>b</sup> (M min <sup>-1</sup> ) | $V_M$ (M min <sup>-1</sup> ) | $k_{\text{cat}}$ (h <sup>-1</sup> ) | $K_M$ (M)              | Calc. rate ( $V_0$ ) <sup>c</sup> | $V_0/\text{rate}$ |
|---|----------------------|------------------------|---|--|------------------------------|-------------------------------------|------------------------|-----------------------------------|-------------------|
| <b>Kinetic data calculated by the integrated rate method and reported in the original paper</b> |                      |                        |   |  |                              |                                     |                        |                                   |                   |
| 1   | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.110                                   | $1.20 \times 10^{-6}$                    | $1.05 \times 10^{-4}$        | 125.8                               | $48.92 \times 10^{-4}$ | $5.33 \times 10^{-5}$             | 44                |
| 2   | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.105                                   | $1.09 \times 10^{-6}$                    | $9.91 \times 10^{-5}$        | 118.9                               | $44.00 \times 10^{-4}$ | $5.27 \times 10^{-5}$             | 48                |
| 3   | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.095                                   | $1.04 \times 10^{-6}$                    | $9.56 \times 10^{-5}$        | 114.7                               | $38.12 \times 10^{-4}$ | $5.24 \times 10^{-5}$             | 50                |
| <b>Kinetic data obtained by the initial rate method</b>   |                      |                        |   |  |                              |                                     |                        |                                   |                   |
| 1   | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.110                                   | $1.20 \times 10^{-6}$                    | $2.07 \times 10^{-6}$        | 2.5                                 | $2.32 \times 10^{-3}$  | $1.41 \times 10^{-6}$             | 1.20              |
| 2   | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.105                                   | $1.09 \times 10^{-6}$                    | $2.02 \times 10^{-6}$        | 2.4                                 | $2.80 \times 10^{-3}$  | $1.29 \times 10^{-6}$             | 1.18              |
| 3   | $5 \times 10^{-3}$   | $5 \times 10^{-5}$     | 0.095                                   | $1.04 \times 10^{-6}$                    | $1.83 \times 10^{-6}$        | 2.2                                 | $2.46 \times 10^{-3}$  | $1.23 \times 10^{-6}$             | 1.18              |

<sup>a</sup>The effective concentrations of complex and substrate after mixing are halved with respect to their initial concentrations because both are mixed with equal volumes. <sup>b</sup>Rate has been calculated using  $18\,300\text{ M}^{-1}\text{ cm}^{-1}$  as the molar absorptivity of the product. <sup>c</sup>Calculated rate has been determined using the equation:  $V_0 = \frac{V_M[S]}{[S] + K_M}$ .

We have now calculated the  $k_{\text{cat}}$  values by the “initial rate method” considering the molar extinction coefficient of amino-phenoxazinone (APX) as  $18\,300\text{ M}^{-1}\text{ cm}^{-1}$ . The corresponding rate vs. substrate concentration plots and Lineweaver–Burk plots for three complexes are shown in Fig. 1. The new kinetic parameters of complexes 1–3 are included in Table 2 and the results of these measurements are compared with the previously reported data in Table 3.

(5) The caption of Fig. 9 should be corrected to “Increase of the APX band at around 430 nm after mixing of equal volumes of methanolic solutions of OAP ( $1 \times 10^{-2}\text{ M}$ ) and complex 2 ( $1 \times 10^{-4}\text{ M}$ ). The spectra were recorded at 5 min intervals for 75 min”.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

## References

- 1 L. Gasque, A. Mendieta and G. Ferrer-Sueta, Comment on “Mixed azido/phenoxido bridged trinuclear Cu(II) complexes of Mannich bases: Synthesis, structures, magnetic properties and catalytic oxidase activities”, *Dalton Trans.*, 2018, **47**, 9385–9399 and “Tri- and hexa-nuclear Ni<sup>II</sup>–Mn<sup>II</sup> complexes of a N<sub>2</sub>O<sub>2</sub> donor unsymmetrical ligand: synthesis, structures, magnetic properties and catalytic oxidase activities”, *Dalton Trans.*, 2018, **47**, 13957–13971, *Dalton Trans.*, 2020, DOI: 10.1039/C9DT01498E.

<sup>d</sup>Department of Chemistry, Sri Ramkrishna Sarada Vidyamahapitha, Kamarpukur, West Bengal, 712612, India

