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Correction: Tri- and hexa-nuclear Ni^{II}–Mn^{II} complexes of a N₂O₂ donor unsymmetrical ligand: synthesis, structures, magnetic properties and catalytic oxidase activities

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rsc.li/daltonCorrection for 'Tri- and hexa-nuclear Ni^{II}–Mn^{II} complexes of a N₂O₂ donor unsymmetrical ligand: synthesis, structures, magnetic properties and catalytic oxidase activities' by A. Ghosh *et al.*, *Dalton Trans.*, 2018, 47, 13957–13971.

In response to the overestimation of k_{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, 13957–13971) that has been pointed out by Laura Gasque *et al.*,¹ 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” which was not mentioned in the text. Therefore, the sentence on page 13964, right column should be changed to “The kinetic studies of catecholase-like activity were performed using methanolic solutions of complexes 3 and 4 under aerobic conditions by the integrated rate method”.

(2) To avoid any confusion for readers, the caption of Fig. 7 should be changed to “Increase in the 3,5-DTBQ band at around 400 nm after mixing of equal volumes of methanolic solutions of 3,5-DTBC (1×10^{-2} M) and complex 3 (5×10^{-5} M) (left) and a plot of the rate vs. substrate concentration (right). The inset shows the corresponding Lineweaver–Burk plot of 3. The UV-spectra were recorded at 5 min intervals”.

(3) The Calc. rate/“rate” factors calculated by Laura Gasque *et al.*¹ 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. Therefore, we have recalculated the Calc. rate/“rate” factors for complexes 3 and 4 with the correct concentration of catalyst and with different concentrations of substrate (Table 1). From these calculations, one can see that the Calc. rate/“rate” factors do not exceed ~ 2 for any of these compounds. They are close to ~ 1 for lower concentrations of substrate as expected.

Table 1 Spectral and kinetic parameters of complexes for different substrate concentrations 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] ^a (M)	[Cat] ^a (M)	Δ Absorbance for 5 min ^d	Rate ^b (M min ⁻¹)	V_M (M min ⁻¹)	k_{cat} (h ⁻¹)	K_M (M)	Calc. rate ^c (V_0)	V_0/rate
3	5×10^{-3}	2.50×10^{-5}	0.29	3.583×10^{-5}	4.10×10^{-4}	984	3.31×10^{-2}	5.381×10^{-5}	1.5
	5×10^{-4}	2.50×10^{-5}	0.05	5.767×10^{-6}	4.10×10^{-4}	984	3.31×10^{-2}	6.101×10^{-6}	1.1
4	5×10^{-3}	1.25×10^{-5}	0.35	4.307×10^{-5}	4.34×10^{-4}	2081	3.15×10^{-2}	5.945×10^{-5}	1.4
	5×10^{-4}	1.25×10^{-5}	0.06	6.871×10^{-6}	4.34×10^{-4}	2081	3.15×10^{-2}	6.781×10^{-6}	1.0

^aThe effective concentrations of complex and substrate after mixing are halved with respect to their initial concentrations because both are mixed with equal volumes. ^bThe rate has been calculated using $1630 \text{ M}^{-1} \text{ cm}^{-1}$ as the molar absorptivity of the product. ^cThe calculated rate has been determined using the equation: $V_0 = \frac{V_M[S]}{[S] + K_M}$. ^dFor these compounds the absorbance increases slowly at the beginning of the reaction, then rapidly, and then slowly again at the end of the reaction. Hence, for the rate calculation we took Δ Absorbance for the 5 min time gap at 15–20 min of reaction when the rate appeared to be a maximum.

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(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_{cat} for oxidation of *o*-aminophenol by the “integrated rate method” is a mistake considering the high ϵ 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_{∞} , 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_{cat} values.

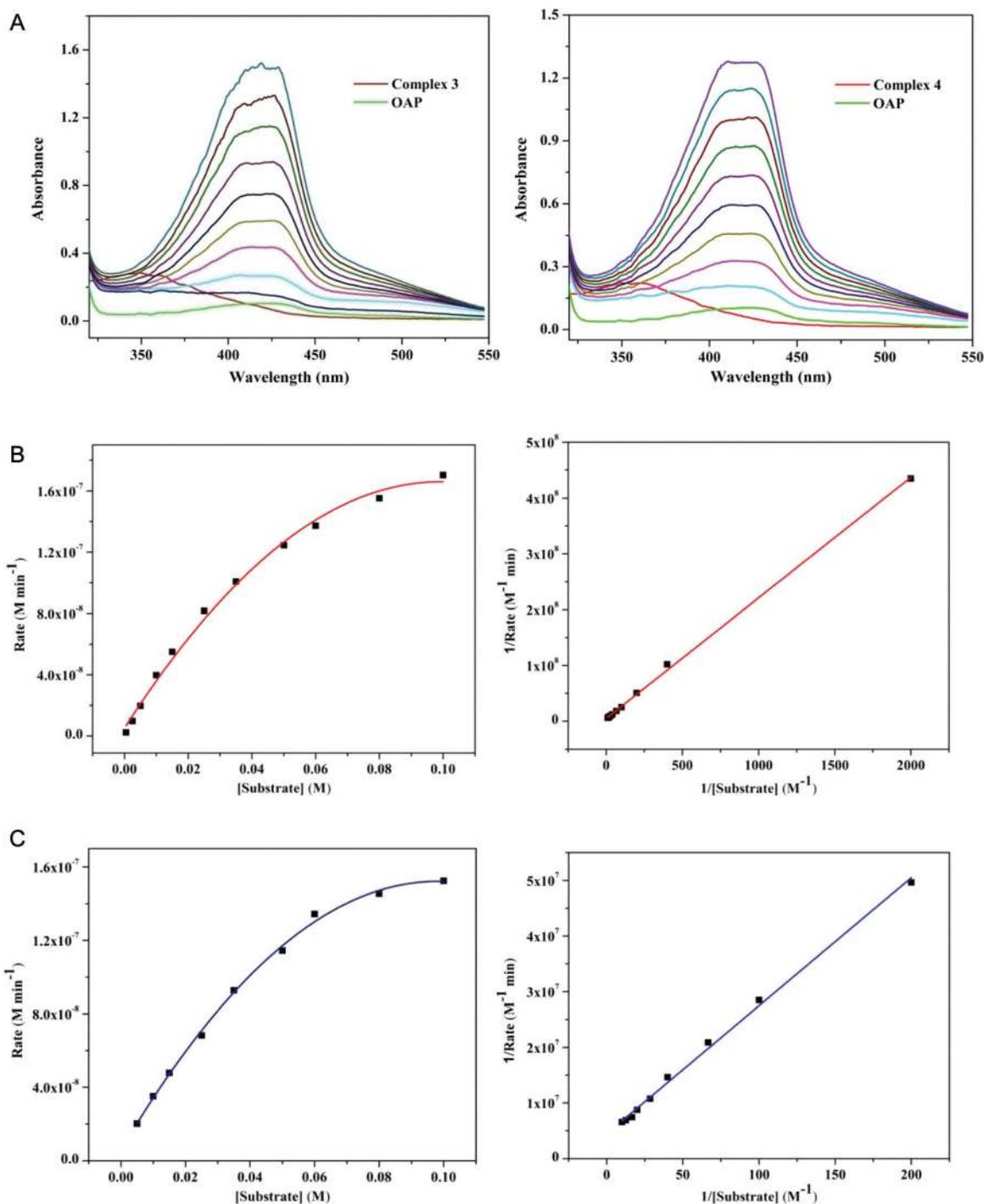


Fig. 1 (A) Increase in absorbance at around 425 nm, after mixing equal volumes of methanolic solutions of *o*-aminophenol (2×10^{-2} M) and complex **3** (2×10^{-5} M) (left) and complex **4** (1×10^{-5} M) (right). The spectra were recorded at 3 min intervals (0–24 min). (B) Plot of the rate vs. substrate concentration (left) and the corresponding Lineweaver–Burk plot (right) for complex **3**. (C) Plot of the rate vs. substrate concentration (left) and the corresponding Lineweaver–Burk plot (right) for complex **4**.



Table 2 Kinetic parameters for the oxidation of *o*-aminophenol catalyzed by complexes 3 and 4

Complex	[S] ^a (M)	[Cat] ^a (M)	ΔAbsorbance for 5 min (0–5 min)	Rate ^b (M min ⁻¹)	V _M (M min ⁻¹)	k _{cat} (h ⁻¹)	K _M (M)	Calc. rate ^c (V ₀)	V ₀ /rate
Kinetic data calculated by the integrated rate method and reported in the original paper									
3	5 × 10 ⁻³	2.50 × 10 ⁻⁵	0.87	9.508 × 10 ⁻⁶	2.65 × 10 ⁻³	6351	1.38 × 10 ⁻²	7.048 × 10 ⁻⁴	74.1
4	5 × 10 ⁻³	1.25 × 10 ⁻⁵	0.56	6.120 × 10 ⁻⁶	2.20 × 10 ⁻³	10 545	1.54 × 10 ⁻²	5.392 × 10 ⁻⁴	88.1
Complex	[S] ^a (M)	[Cat] ^a (M)	ΔAbsorbance for 6 min (0–6 min)	Rate ^b (M min ⁻¹)	V _M (M min ⁻¹)	k _{cat} (h ⁻¹)	K _M (M)	Calc. rate ^c (V ₀)	V ₀ /rate
Kinetic data obtained by the initial rate method									
3	1 × 10 ⁻²	1.0 × 10 ⁻⁵	0.26	2.368 × 10 ⁻⁶	1.34 × 10 ⁻⁵	81	5.15 × 10 ⁻²	2.179 × 10 ⁻⁶	0.92
4	1 × 10 ⁻²	5.0 × 10 ⁻⁶	0.24	2.186 × 10 ⁻⁶	1.19 × 10 ⁻⁵	142	4.27 × 10 ⁻²	2.258 × 10 ⁻⁶	1.03

^aThe effective concentrations of complex and substrate after mixing are halved with respect to their initial concentrations because both are mixed with equal volumes. ^bThe rate has been calculated using 18 300 M⁻¹ cm⁻¹ as the molar absorptivity of the product. ^cThe calculated rate has been determined using the equation: $V_0 = \frac{V_M[S]}{[S] + K_M}$.

Therefore, we have repeated the experiments for the phenoxazinone synthase-like activity of both complexes 3 and 4 with different concentrations of substrate and catalyst, and the *k*_{cat} values have been calculated by the “initial rate method” considering the molar extinction coefficient of amino-phenoxazinone (APX) as 18 300 M⁻¹ cm⁻¹. We obtained nearly linear fits for both compounds with the new data. The plots in Fig. 1A show the increase in the absorbance band at around 425 nm with time due to the formation of amino-phenoxazinone for complexes 3 and 4 with the catalyst concentrations used for determination of the kinetic parameters. The corresponding rate vs. substrate concentration plots and Lineweaver–Burk plots for complexes 3 and 4 are shown in Fig. 1B and C, respectively. The new kinetic parameters are included in Table 2 and are compared with the previously reported data.

(5) The caption of Fig. 8 should be corrected to “Increase in the amino phenoxazinone band at around 425 nm after mixing of equal volumes of methanolic solutions of *o*-aminophenol (1 × 10⁻² M) and complex 3 (5 × 10⁻⁵ M) (left) and plot of the rate vs. substrate concentration (right). The inset shows the corresponding Lineweaver–Burk plot of 3. The UV-vis spectra were recorded at 5 min intervals”.

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^{II}–Mn^{II} complexes of a N₂O₂ donor unsymmetrical ligand: synthesis, structures, magnetic properties and catalytic oxidase activities”, *Dalton Trans.*, 2018, 47, 13957–13971, *Dalton Trans.*, 2020, DOI: 10.1039/C9DT01498E.

