



A journal for new directions in chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. A. A. Huerta, J. Narayanan, J. A. Balderas López, M. Flores-Alamo, E. F. V. Contreras, K. A. L. Gastélum, F. Rocha Alonso, C. B. Palacios Cabrera and A. J. S. Cuevas, *New J. Chem.*, 2020, DOI: 10.1039/C9NJ04027G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

8 9 10

11

12

ģ6

42

43

44

45

46

47

48

49

50

51

52

53

54

55

57

58

59

60

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Enhanced photocatalytic degradation of 2-thiobenzimidazole by *Tris*(8-quinolinolato)cobalt(III) complex through peroxide adduct formation: Theoretical and experimental investigation

Carlos Alberto Huerta Aguilar^a, Jayanthi Narayanan^a*, José Abraham Balderas López^b, Marcos Flores-Alamo^c, Enrique Fernando Velázquez Contreras^d, Karla Alejandra López Gastélum^d, Fernando Rocha Alonzo^d, Cristian Brayan Palacios Cabrera^a, Alan Javier Santiago Cuevas^a

Abstract

Photo-initiated oxidative degradation of 2-thiobenzimidazole (2-TBI) was studied using different semiconducting metal complexes derived from 8-hydroxyquinoline of the general formula, $[MQ_3C_2H_5OH]$ [Q= 8-quinolinolato anion; M= Cr³⁺, (**CrQ3**); Co³⁺, (**CoQ3**); Fe³⁺, (**FeQ3**)]. The degradation kinetics was monitored by UV-vis spectroscopy perceiving the changes in absorbance of subtract. The effect of pH and visible light irradiation on degradation was studied observing a significant increment in the oxidation rate with the presence of visible light whenever **CoQ3** is used as a catalyst. By using density functional theory (DFT), it was found that the transition state energy of the adduct formed between **CoQ3** and H₂O₂ is very low compared with other studied catalysts, which activates the formation of 'OH radicals from H₂O₂ increasing 2-TBI degradation rate. In addition, a thermodynamically feasible degradation mechanism was proposed by calculating energy barriers involved in the 2-TBI oxidation pathway.

1. Introduction

Metal complexes of Schiff base ligands are considered in the photocatalytic reactions owing to their interesting photophysical properties that indorse the excited-state metal complexes experience unusual structural and electronic changes generating Fenton-like catalytic reactions.¹⁻⁷ Thus, in photo/Fenton reactions, metal complex reacts with H_2O_2 under UV light to generate 'OH radicals, which induce the oxidation process increasing its velocity.^{3, 8-12} Recent studies

show that significant modifications in the structure of metal complex exhibit a considerable advancement for the oxidation processes.¹³⁻¹⁷ For example, Schiff base metal complexes which are highly photoactive, involve very strongly in the production of Reactive Oxygen Species (ROS) that can be employed in the degradation of organic contaminants.¹⁸ Therefore, it has been considered that the catalytic oxidation is highly related with structure of the metal complex, type of ligands, and oxidation state of metal ions; besides pH, solvent medium, the concentration of substrate or catalyst are crucial factors. $^{\rm 19\mathchar`22}$ However, bandgap energy of the metal complex plays a crucial role since that determine the amount of energy required to produce photo-excited electron-hole pairs; it has not been much focused in the literature.²³⁻²⁷ Therefore, the study of HOMO-LUMO influenced photocatalytic efficiency of the metal complex with activation energy barriers involved in the oxidation process is still a topic of interest. Hence, to understand the mechanism of photo-induced electron/ energy transfer in the photocatalytic degradation process, study of CB and VB alignment of the photocatalysts with reference to the activation energy that involved in the formation of ROS is important.^{23, 28} Thus, the present work deals with the oxidation of 2-thiobenzimidazole (2-TBI) by different metal complexes

^a División de Ingeniería en Nanotecnología, Universidad Politécnica del Valle de México, Av. Mexiquense s/n esquina Av. Universidad Politécnica, Tultitlan,

Estado de México, C.P. 54910, México.

^b Instituto Politécnico Nacional-UPIBI, Avenida Acueducto S/N, Col. Barrio la Laguna,

⁵⁶ Del. Gustavo A. Madero, C. P. 07340, CDMX, México.

^c Facultad de Química, Universidad Nacional Autónoma de México,

Ciudad Universitaria, Coyoacán 04510, México D.F., México.

^d Departamento de Investigación en Polímeros y Materiales, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, Hermosillo, Sonora, México.

Contact e-mail address: jnarayanan@upvm.edu.mx

ARTICLE

under visible light irradiation, and bandgap energy of the metal complexes is correlated with their catalytic efficiency using DFT. The use of 2-TBI has been increased in several industries such as pharmaceuticals, pesticides, rubber, etc., consequently, a large quantity of this compound is being released into the surroundings, and it is persistent in the environments due to its poor water-solubility.²⁹⁻³³ Schiff base complexes of Cr³⁺, Co³⁺, and Fe³⁺ with 8-hydroxyquinoline were prepared and used for the oxidation of 2-TBI by H_2O_2 under visible light. A mechanism for this degradation process is proposed by analysing the degraded products. In addition, the thermodynamic feasibility of the mechanism was analysed by DFT.

2. Experimental

2.1. Materials and instruments

All reagents purchased from Aldrich Chemical & Co used as received, and solvents were distilled before using in the experiments. Elemental (C, H and N) analyses were carried out on using Fissions (Model EA 1108 CHNS-O). For all samples, Fourier transformed infrared (FTIR) spectra in the range of 4000-400 cm-1 were recorded on a Perkin Elmer Frontier FTIR instrument. 1H NMR spectra was recorded on Varian VNMRS equipment (300 MHz) by using DMSO as an internal standard. Powder X-ray diffraction (XRD) analysis were performed on a D8 Advance Da Vinci equipped with a Bruker AXS theta-theta configuration with CuKα (I= 1.54 Å). UV-Vis spectrophotometer (Perkin-Elmer Lambda 25) was employed to analyse the electronic properties for the complexes and used to monitor the oxidation of 2-TBI. The intermediates formed from the oxidation of 2-TBI were identified by a chromatographic technique (Agilent 1200 HPLC equipped with a 150 mm Zorbax C-18 column) coupled to a 6410 MS ESI+ detector.

2.2. Degradation of 2-TBI

The degradation of 2-TBI was performed by different complexes under visible light, the results were compared with those obtained without the light irradiation, and the effect of pHs (7 \pm 0.5 and 4 \pm 0.5) was studied. Typically, metal complex (0.05 mM) used to oxidize the substrate (2-TBI, 0.05 mM), in H2O2 (0.5 % v/v) in an aqueous solution under visible light. The concentration of the substrate was monitored by UV-Vis absorption profile by measuring the intensity of 2-TBI and recorded in the range between 200 and 350 in different time intervals. The light source for the irradiation was 800 lm, 60 W tungsten lamp. During the oxidation study, characterization of the reaction intermediates were carried out by NMR and GC/MS techniques.

2.3. Crystallographic studies

Crystal structure of CoQ3 was resolved by X ray diffraction technique on Oxford Diffraction Gemini "A" diffractometer

using a CCD area detector ($\lambda_{MoKa} = 0.71073_{Victual Agraphine}$ monochromator) equipped with a sealed dube X323V3000000 at 130 K. The crystal-to-detector distance was 55 mm. Crystal

Journal Name

monochromator) equipped with a sealed tube 1X3Gay source at 130 K. The crystal-to-detector distance was 55 mm. Crystal unit cell was determined with a set of 15/3 narrow frame/runs (1° in 2) scans. A data set of 225 frames of intensity data was collected, and integrated by using an orientation matrix by CrysAlisPro and CrysAlis RED software packages employing the narrow frame scans. Final cell constants were determined with using total 3486 reflections for the structural refinement (\square < 29.461°). Collected data were corrected using analytical numeric absorption by considering a multifaceted crystal model.³⁴ The structure was solved using a dual-space algorithm method with SHELXT-2014 and by full-matrix least squares refinement was performed by minimising (Fo2-Fc2)2 using SHELXL-2014 in the WinGX program packages.³⁵⁻³⁷ All non-hydrogen atoms were refined anisotropically; the H atoms bound to ethanol molecule were located from difference Fourier maps and refined as riding with Uiso(H) = 1.5Ueq(-OH). The H atoms attached to the C atoms were placed in geometrically idealized positions and refined using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueg(- CH_{2} , CH_{2}) and $Uiso(H) = 1.5Ueq(-CH_{3})$. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary material number CCDC 1904242. Copies of the data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; P: +44 (0)1223 336408: F: +44 (0)1223 336033; email:deposit@ccdc.cam.ac.uk.

2.4. Computational studies

To understand the electron migration mechanism from the metallic centre of the complex to H_2O_2 , and the formation of intermediates from the substrate, theoretical calculations based on Density Functional Theory (DFT) were carried out using Gaussian 16 software.³⁸ The geometry of all the metal complexes was optimized; the energy of its ground state and the first excited state was calculated by using its corresponding spin multiplicity. All ground-state calculations were performed using a uB3LYP/LANL2DZ hybrid basis set while the Time-Dependent (TD-DFT) calculations with the aforementioned methods were used for the first (S0 \rightarrow S1) excited state processes.³⁹ The structure of the ligand was fully optimized and the corresponding data were then used as input for the optimization of each metal complex. To understand the molecular orbital contribution to the electronic absorption bands for the metal complexes, TD-DFT was employed using water as a solvent given by IEF-PCM electrostatic solvent model. Additionally, the charge distribution in the structures was analysed by Natural Population Analysis (NPA).⁴⁰ Internal Reaction Coordinate (IRC) parameters such as Activation Energy (E_a), and Transition States (TS) were elucidated using a BBK95 functional and a QST3 guess method with a subsequent TS optimization.⁴¹ The thermodynamic feasibility of the optimized TS was determined through IRC calculation.

```
[CrQ3·C<sub>2</sub>H<sub>5</sub>OH] (CrQ3)
```

3

4

5

6

7

8

9

10

11

12

13

194 1970 10

55:570707/27/2002/12/2002/12/2002/12/2002/12/2002/27/2002/27/2002/27/2002/27/2002/27/2002/27/2002/27/2002/27/20

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60

Journal Name

The preparation of CrQ3 is followed as reported previously.⁴² To a ligand 8-HQ (0.436 g, 3.0 mmol) dissolved in an ethanol (200 mL) containing NaOH (0.12 g, 3.0 mmol), CrCl₃·6H₂O (0.266 g, 1.0 mmol) in ethanol was added; the resulting solution was kept at 30°C for 24 hrs, observing a colour change from green to dark red. A reddish brown precipitate was obtained after removing solvent by roto-evaporator; it was recrystallized from a solvent mixture of acetonitrile and absolute ethanol (1:1, v/v) to yield bright reddish-brown crystals. Elemental analysis: anal. calc. (%) for C29H24CrN3O4: C, 65.65; H, 4.56; N, 7.92; found (%): C, 65.60; H, 4.44; N, 7.89. FT-IR (v_{max}/cm^{-1}) (Fig. S1): bending vibrations at 520_{vs}, 616_s (pyridine in coordination ring formation), $1373_{vs} \delta[O-H]$, $1462_{vs} \delta[\alpha-CH_2]$, and pyridine ring stretching vibration at 1497_{vs} were assigned. Other signals in the FT-IR spectrum were 1571_s [v(C=C)], 1321_s [(v(C-H)], and 1277_m [(v(C=N)]. ¹H NMR (Fig. S2) (DMSO-d⁶, 300MHz) δ (s: singlet, d: doublet, t: triplet, q: quintet, m: multiplet): 8.75 (d, 1H), 8.23 (d, 1H), 7.45 (t, 1H), 7.40 (t, 1H), 7.28 (d, 1H), 7.05 (d, 1H), 4.87 (q, 2H), 3.31 (m, 1H), 1.2 (t, 3H).

$[CoQ3 \cdot C_2H_5OH] \text{ (CoQ3)}$

To an ethanolic solution (200 mL) of the ligand 8-HQ (0.436 g, 3.0 mmol) containing NaOH (0.12 g, 3.0 mmol), CoCl2·6H2O (0.238 g, 1.0 mmol) in ethanol was added, and the resulting solution was reflexed for 24 hrs at 30 °C, observing a colour change from violet to red. A red precipitate obtained was further recrystallized from a solvent mixture of acetonitrile and absolute ethanol (1:1, v/v) to obtain the deep red crystals, which was suitable for X-ray analysis. Elemental analysis: anal. calc. (%) for C₂₉H₂₄CoN₃O₄: C, 64.80; H, 4.50; N, 7.82; found (%): C, 64.86; H, 4.46; N, 7.90. FT-IR (v_{max}/cm^{-1}) (Fig. S1): bending vibrations at 819m [=C-H & =CH2]_{out of plan}, and very weak ring wagging vibrations at 910_{vw} [CH2=CH- and -CH2]_{out of} $_{\mbox{plane}}$ were consigned. Also, bending vibrations at $733_{\mbox{m}}$ and 778_m (O-H_{out of plan}), 1318w (O-H_{bending in plan}), 1462_m ($\alpha\text{-CH}_2$ bending), and a strong pyridine ring stretching vibrations at 1497s and 1574_m were observed. ¹H NMR (Fig. S2) (DMSO-d⁶, 300MHz) δ (s: singlet, d: *doublet*, t: *triplet*, q: *quintet*, m: multiplet): 8.75 (d, 1H), 8.27 (d, 1H), 7.50 (t, 1H), 7.40 (t, 1H), 7.3 (d, 1H), 7.1 (d, 1H), 5.1 (q, 2H), 3.27 (m, 1H), 1.2 (t, 3H).

[FeQ3·C₂H₅OH] **(FeQ3)**

To a ligand 8-HQ (0.436 g, 3.0 mmol) dissolved in an ethanol (200 mL) containing NaOH (0.12 g, 3.0 mmol), FeCl₃·6H₂O (0.270 g, 1.0 mmol) in ethanol was added; the resulting solution was stirred for 30 min, observing a colour change from brown to black. A black precipitate after removing the solvent by roto-evaporator was re-crystallized from absolute ethanol. Elemental analysis: anal. *calc*. (%) for C₂₉H₂₄FeN₃O₄: C, 65.18; H, 4.53; N, 7.86; *found* (%): C, 65.01; H, 4.56; N, 7.88. FT-IR (v_{max}/cm⁻¹) (Fig. S1): very strong stretching vibrations at 562_{vs} [pyridine ring deformation], 1276_{vs} [(v(C=N)], and 1320_{vs}, 1572_m [(v(C-H)] were observed. Also, the following strong bending vibrations, 736_{vs} δ [O-H]_{out of plan}, 821_{vs} δ [CH2=CH], 1105_{vs} δ [C-O-H]_{quinoline}, and 1376_{vs} δ [O-H] confirm the formation coordination sphere in **FeQ3**. ¹H NMR (Fig. S2) (DMSO-d⁶, 300MHz) δ (s: *singlet*, d: *doublet*, t: *triplet*, q:

quintet, m: multiplet): 9.01 (d, 1H), 8.92 (d, 1H), $\sqrt{2}$ 98 (t, 1H), 7.75 (t, 1H), 7.59 (d, 1H), 7.45 (d, 1H), 4.9 (a, 12H), 33/30 (m/ 1H), 1.01 (t, 3H).

3. Results and discussions

3.1. FTIR spectra

The IR frequencies (λ_{max} /cm⁻¹) of ligand 8-HQ determined with those of metal complexes (Table S1), observed a remarkable shift in the frequency for the complex from the ligand (Fig. S1). For example, u(O-H) stretching vibrations at 3034 and 709 cm⁻¹ from the phenolic group observed for 8-HQ were disappeared; OH stretching vibrations due to the intramolecular hydrogen bonding were observed in the range, 3200–3500 cm⁻¹ for the complex systems.⁴³⁻⁴⁴ Similarly, $[u(C=N)_{py}]$ stretching vibration detected at 1580 cm⁻¹ for 8-HQ was shifted to 1572-1574 cm⁻¹ for the metal complexes, revealing the involvement of imine nitrogen in chelation with the metal ion.⁴⁵⁻⁴⁶ Also, the aromatic C=C stretching vibration of benzene at 1501 cm⁻¹ for 8-HQ was shifted to 1495-1497 cm⁻¹ in the presence of metal ions, suggesting the presence of distortion in the benzene ring caused by the coordination of hydroxyl oxygen atom with the metal ion. Besides, all the metal compounds showed the following ring deformation vibrations: α (-CH₂), 1462 cm⁻¹; υ (C-H), 1318 to 1321 cm⁻¹; u(=C-H and =CH₂ out-of-plane), 800-821 cm⁻¹, which were not observed in the ligand alone confirms the involvement of 8-HQ in the metal chelation.

3.2. X-ray structure analysis of [Co(8-quinolinolato)₃·C₂H₅OH]

Crystals of $[Co(8-quinolinolato)_3 \cdot C_2H_5OH]$ were grown in ethanol at room temperature; the crystal structure was resolved by single crystal X-ray diffraction analysis at T = 130 K. A perspective view of the molecular structure of **CoQ3** is shown in figure 1, and the crystal data and refinement details are given in Table 1. Selected bond lengths and bond angles are shown in table 2 that are consistent with the previously reported data at room temperature.⁴⁷ In complex **CoQ3**, the six-membered chelate ring has been created around the Co^{III} atom by three 8-quinolinolato anions through an asymmetric meridional arrangement along with one ethanol molecule forming a slightly distorted octahedral structure.

New Journal of Chemistry Accepted Mai

Journal Name





ARTICLE

Fig. 1 ORTEP drawing of the asymmetric unit of [Co(8-quinolinolato)_3 C_2H_5OH] with thermal ellipsoids drawn at the 50% of probability.

The average N, O bite angle 85.90°, the exclusive meridional geometry of the isolated CoQ3 is similar to other chelates of this type.⁴⁸ The observed Co^{III}–N bond distances [1.918(2)–1.937(2) Å] are longer than the Co^{III}–O [1.898(1)–1.906(1) Å] and are comparable to other 8-quinolinolate complexes.⁴⁹ The planar 8-quinolinolato monovalent anions are nearly perpendicular to each other where the chelate rings, Co1/O1/C1/C22/N1, Co1/O2/C10/C11/N2, and Co1/O3/C19/C20/N3 make dihedral angles of 87.05(7), 87.67(9) and 87.23(7) °, respectively.

In the crystalline arrays (Fig. 2), intermolecular interactions of type π - π through hydrogen bonds, O—H···O and C—H···O are observed. For example, an oxygen atom (ethanol molecule) involves hydrogen bond formations such as O4—H4···O2 (1.858 Å), C8—H8···O4 (2.717 Å), and C18—H18···O4 (2.650 Å) (Table 3). The overlapping arrangement of neighbouring parallel 8-quinolinolato rings was seen at 4.608 Å for Cg5-Cg8, and 4.045 Å for Cg9—Cg9 (Cg5= centroid C11—N12/C15, Cg8= centroid C10/C18 and Cg9=C19/C27), with the existence of π - π stacking between the neighbouring complex molecules.



Fig. 2 Crystal array of $[Co(8-quinolinolato)_3 C_2H_5OH]$, view along the b-axis and with perspective to plane formed by a-c axes emphasizing the C11(9), R11(6) motif's.

Table 1	Crystal	data	and	structure	refinement	for	compound
[Co(8-q	uinolino	lato)₃	C_2H_5	OH].			

Empirical formula	$C_{29}H_{24}CoN_3O_4$
Formula weight	537.44
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 11.1941(6) Å
	b = 12.9126(7) Å
	c = 16.5167(9) Å
	β= 93.965(5)°.
Volume	2381.7(2) Å ³
Z	4
Density (calculated)	1.499 Mg/m ³
Absorption coefficient	0.764 mm ⁻¹
F(000)	1112
Crystal size	0.500 x 0.130 x 0.080 mm ³
Theta range for data collection	3.363 to 29.461°.
Index ranges	-14<=h<=13, -
	17<=k<=15, -22<=l<=20
Reflections collected	13622
Independent reflections	5633 [R(int) = 0.0440]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Analytical
Max. and min. transmission	0.942 and 0.775
Refinement method	Full-matrix least-squares
	on F ²
Data / restraints / parameters	5633 / 1 / 338
Goodness-of-fit on F ²	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1116
R indices (all data)	R1 = 0.0877, wR2 = 0.1298
Largest diff. peak and hole	0.915 and -0.723 e.Å ⁻³

Journal Name

Table 2 Selected bond lengths [Å] and angles [°] for compound [Co(8-quinolinolato)₃[.]C₂H₅OH].

 $\alpha = \gamma \neq \beta$ for **CrQ3**, **CoQ3**, and **FeQ3** suggest monoclinic crystal structure of P type, and these results are well coincide with χ_7 ray structural data of these similar type compounds.^{42-44, 53-54}

	Bond lengths [Å]		Bond angles [°]
C(1)-O(1)	1.328(4)	O(3)-Co(1)-O(1)	90.22(9)
C(10)-O(2)	1.338(3)	O(3)-Co(1)-O(2)	92.05(9)
C(19)-O(3)	1.322(3)	O(1)-Co(1)-O(2)	176.74(8)
C(28)-O(4)	1.368(5)	O(3)-Co(1)-N(2)	86.70(10)
C(28)-C(29)	1.569(7)	O(1)-Co(1)-N(2)	91.94(10)
Co(1)-O(3)	1.890(2)	O(2)-Co(1)-N(2)	85.87(10)
Co(1)-O(1)	1.902(2)	O(3)-Co(1)-N(1)	175.92(10)
Co(1)-O(2)	1.913(2)	O(1)-Co(1)-N(1)	85.71(10)
Co(1)-N(2)	1.918(2)	O(2)-Co(1)-N(1)	91.99(10)
Co(1)-N(1)	1.934(3)	N(2)-Co(1)-N(1)	93.09(10)
Co(1)-N(3)	1.937(2)	O(3)-Co(1)-N(3)	86.12(10)
O(4)-H(4D)	0.914(19)	O(1)-Co(1)-N(3)	91.98(9)
C(1)-C(2)	1.420(4)	O(2)-Co(1)-N(3)	90.50(9)
C(1)-C(9)	1.391(4)	N(2)-Co(1)-N(3)	171.83(11)
C(7)-C(8)	1.368(5)	N(1)-Co(1)-N(3)	94.35(10)

Table 3 Geometrical parameters for the intermolecularhydrogen bonding interactions in the crystal structure of $[Co(8-quinolinolato)_3+C_2H_5OH]$ [Å].

D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)
C(3)-H(3)O(2)	0.95	2.52	2.994(4)	110.8
C(4)-H(4)O(2)#1	0.95	2.61	3.270(4)	127.3
C(12)-H(12)O(1)	0.95	2.47	2.945(4)	110.9
C(18)-H(18)O(4)	0.95	2.65	3.284(4)	124.6
C(21)-H(21)N(1)	0.95	2.64	3.100(4)	110.5
O(4)-H(4D)O(2)	0.914(19)	1.86(2)	2.741(3)	163(5)
Symmetry transform	atoms: #1			
1/2,-z+1/2.				

3.3. XRD patterns of synthesized metal complexes

Powder XRD patterns of the complexes were performed in the range ($2\theta = 10-80^{\circ}$) (Fig. 3). The phase purity and sharp peaks for all the compounds indicating the crystalline nature of these complexes. The independent indexing of major refluxes was carried out using least square method. The miller indices *h*, *k*, *l* were calculated and refined by using Match software. The *d* values were obtained by Bragg's equation ($n\lambda = 2dsin\theta$) using the values of sin 2θ considering *h*, *k*, *l* data.⁵⁰⁻⁵² The correction of *d*-values was confirmed by comparing the observed density with that calculated from the X-ray powder diffractogram. The lattice constants a, b and c for each unit cell were found out and are given in Table 4. The lattice parameters as $a\neq b\neq c$ and





anusc

mistry Accepted M

Journal Name

Table 4 Lattice constant, unit cell volume, crystal system, interplanar spacing of metal complexes.

Metal	Lattice constants (Å)			Inter axial	Unit cell	Crystal	Angle	d value	
complex	A	b	с	ungie	(ų)	System	(20)	(Ă)	
CrQ3	10.98	11.43	12.67	α=γ=90≠β	1590.1	Monoclinic	12.21	7.24	
CoQ3	10.14	10.87	11.76	α=γ=90≠β	1296.21	Monoclinic	10.55	8.38	
FeQ3	9.96	10.27	11.23	α=γ=90≠β	1148.71	Monoclinic	10.27	8.6	

3.4. Electronic spectra

ARTICLE

1

Electronic absorption spectra were recorded for all the metal complexes in ethanol or in DMF (1.0 x 10^{-3} M, at 25 °C) as shown in figure 4.



Fig. 4 UV-Vis absorption spectra for the metal complexes $(1.0 \times 10^{-3} \text{ M})$ at 25° C. [DMF = N,N-dimethylformamide].

UV-Vis spectra recorded for the metal complexes shows intense absorption bands in the range of 206 to 251 nm corresponding to $n \rightarrow \pi^*$ (C=N)_{py}, and $\pi \rightarrow \pi^*$ transitions; the ligand-to-metal charge-transfer (LMCT) bands at 250-300 nm which were originated by coordination of 8-HQ with metal center.55-57 In addition, d-d transitions for all the complexes were observed in the visible region, for example, CrQ3 presents three bands (260, 316 and 398) corresponding to the ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)(\upsilon_{3}),$ ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)(\upsilon_{2}),$ transitions, and ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}(F)(u_1)$ respectively. Similarly, for **CoQ3**, typical *d*-*d* transitions, ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}(D)(\upsilon_1)$ (312 nm) and 1A1g \mathbb{P} 1T2g(D)(υ_2) (386 nm) for low spin octahedral Co³⁺ (d⁶) were observed. In the case of FeQ3, an intense charge transfer band associated with bathochromic shift of ligand to metal charge transfer (LMCT) at 291 nm for ${}^{2}T_{2g} \rightarrow {}^{4}T_{2g}(D)(\upsilon_{3})$ which almost mask the d-d bands was observed.⁵⁸ In addition, spin and multiplicity forbidden transitions exhibit as weak bands at 360, 450, and 590 nm which are corresponding to ${}^{2}T_{2g} \rightarrow {}^{4}T_{1g}(G)(\upsilon_{1})$, $2T2g \rightarrow 4T2g(G)(\upsilon_1), \text{ and } {}^2T_{2g} \rightarrow {}^4A_{1g}(G), {}^4E_g(G)(\upsilon_2) \text{ respectively}$ confirm the presence of low spin octahedral Fe³⁺ (d⁵).

To analyse the semiconductor nature of the metal complex, direct and indirect bandgap (E_g) were incalculated of from absorption spectra by plotting electronic parameters for *Tauc's* exploration (*Tauc's* expression vs. energy), (Fig. 5).⁵⁹

Direct bandgap: $(\alpha h v)^2$ (1)

Indirect bandgap: $(\alpha h \upsilon)^{1/2}$ (2)

The absorption coefficient (α), Plank constant (h), and photon's frequency (υ) were used to determine E_g from the extrapolated linear plot. The absorption coefficient (α) is determined by relating photon energy (h*neo) as follows:

 $\alpha = \beta/(h\upsilon)(h\upsilon-Eg)^n$ Or $(\alpha h\upsilon)^{1/n} = \beta(h\upsilon-Eg)$

E_g: optical bandgap energy and n: power factor of the transition mode depending upon the nature of the material whether it is crystalline or amorphous. *Tauc's* plotting for $(\alpha h \upsilon)^{1/2}$ versus the photon energy $(h \upsilon)$ results a straight line at specified region, and the extrapolation of that straight line intercepting the $(h \upsilon)$ -axis was considered as indirect optical energy gap (E_g).



Fig. 5 Bandgap energies for the metal complexes by *Tauc's* plot. a) direct; b) indirect.

The observed variation in the direct and indirect bandgap (Fig. 5) of metal complexes indicating the amount of energy required to produce photo-excited electron-hole pairs and its degree of delocalization of each metal complexes that involve in the photo-reduction of H2O2.

3.5. Photocatalytic studies

The photocatalytic activities of the metal complexes were studied on 2-TBI oxidation by using hydrogen peroxide as oxidant. Typically, oxidative degradation of an aqueous solution of 2-TBI (50 mL, 0.05 mM) using each complex (5.0 mM) along with H2O2 (3mL of 30% soln.) was studied under visible light (40W bulb). The observed absorbance changes during 2-TBI degradation were recorded at $\lambda_{max}/300$ nm for 3

3

4

5

6

7

8

9

10

11

12

13

194 1970 10

55:570707/27/2002/12/2002/12/2002/12/2002/12/2002/27/2002/27/2002/27/2002/27/2002/27/2002/27/2002/27/2002/27/20

> 42 43

> 44

45 46 47

48

49 50 51

52

53

54

55

56

57

58

59 60

Journal Name

hours (Fig. 6). The concentration of substrate was measured in constant time intervals, and it was plotted against time. The same experimental procedure was followed when the 2-TBI degradation was carried out without the presence of light irradiation. The rate constant for the oxidation was determined in the presence of each complex, and compared each other. Furthermore, the effect of pH on the determined rate constant was analysed using neutral pH=7.0±0.5, and acidic pH=4.0±0.5 conditions using HNO₃. Similarly, the effect of temperature on the oxidation was studied observing the decomposition of hydrogen peroxide at the higher temperatures; therefore, 25 °C was considered as optimum reaction temperature for 2-TBI degradation.

A decrease of band intensity at 300 and 290 nm corresponding to the transitions, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively for 2-TBI was observed during the oxidation, and a new signal at 276 nm was appeared simultaneously with an isosbestic point at 282 nm, indicating the formation of new degraded products (Fig. 6). Kinetic parameters obtained for 2-TBI degradation under different experimental conditions are summarized in Table 5. The photocatalytic efficiency of metal complexes were compared with Fenton reagent using H₂O₂ as oxidant under the same experimental conditions.



Fig. 6 Changes in absorption profile of 2-TBI during the oxidative degradation.



Fig. 7 *Pseudo* first order kinetics for 2-TBI during the degradation by different metal complexes at neutral pH ($pH=7.0\pm0.5$) without the visible light irradiation.



Fig. 8 *Pseudo* first order kinetics for 2-TBI during the degradation by different metal complexes at neutral pH ($pH=7.0\pm0.5$) under visible light irradiation.

In both the studied pH conditions (pH7_{light}, Fig. 7; pH7_{without light}, Fig. 8; pH4_{light}, Fig. S3; pH4_{without light}, Fig. S4), catalyst alone cannot oxidize 2-TBI without using H₂O₂ as oxidant; the fitted linear lines (R2 > 0.9) indicate that 2-TBI degradation follows pseudo-first-order kinetics. In the observed 2-TBI oxidation kinetics, pH of the reaction medium and visible light irradiation have a significant effect on its degradation. Figures, 9, 10, and 11 show the comparison of catalytic efficiency of all the studied metal complexes at different experimental conditions.

ARTICLE

Journal Name

ARTICLE

1 2

3

4

5

6

7

8

9

10

11

12

Bablished on 2 U February 2020, Dewnbadeddyr KA (17R, 08K, 19K) (1872) 2220202:53 10682405, 1070

Generally, acidic pH showed a shrink in the 2-TBI degradation for all the metal complexes due to the protonation of electrondonating groups in the metal complex slowing the excitation of electrons from metal ion. At neutral pH conditions, all the metal complexes showed an improved 2-TBI degradation rate along with percentage removal. Similarly, visible light irradiation favours the oxidation to take place rapidly increasing degradation percentage for all the studied catalysts. Among the studied catalysts, **CoQ3** showed a higher velocity rate ($1.06 \times 10^{-3} \text{ s}^{-1}$ with $t_{1/2}$ of 653.91 s) with 99.1% removal of 2-TBI, indicating the degradation is more effective over **CoQ3** under visible light irradiation.

Table 5 Kinetic parameters for the degradation of 2-TBI by metal complex catalysts under different experimental conditions.

Oxidation conditions	Catalyst	T½ (s)	k (s ⁻¹)	R ²	2-TBI Removal (%)
	CrQ3	956.0651	7.25E-04	0.9491	68.7
	FeQ3	780.2783	8.88E-04	0.9451	83.3
pH4 With Light	CoQ3	639.8282	1.08E-03	0.9558	83.8
	H_2O_2	1248.5	5.55E-04	0.9235	85.6
	Fenton	1252.676	5.53E-04	0.921	89.5
	CrQ3	753.4208	9.20E-04	0.9199	68
nH4	FeQ3	812.2819	8.53E-04	0.9463	83.7
Without	CoQ3	732.1977	9.47E-04	0.9606	88.9
light	H_2O_2	1542.9	4.49E-04	0.901	79.6
	Fenton	1200.601	5.77E-04	0.8789	83
	CrQ3	714.5847	9.70E-04	0.9806	87.7
	FeQ3	850.4873	8.15E-04	0.9396	80.4
pH7 With light	CoQ3	653.9124	1.06E-03	0.9427	99.1
	H_2O_2	812.2819	4.80E-04	0.9991	81.6
	Fenton	558.2393	1.24E-03	0.9572	92.3
	CrQ3	709.707	9.77E-04	0.9074	75.4
nH7	FeQ3	896.311	7.73E-04	0.9307	73.2
Without	CoQ3	859.2	8.07E-04	0.9969	93.5
light	H_2O_2	1386.294	5.00E-04	0.9423	93.8
	Fenton	1551.81	4.47E-04	0.9649	90.65

- 52 53 54 55 56 57
- 58 59
- 59 60



Fig. 9 Comparison of rate constants for the oxidation of 2-TBI by metal complexes at different experimental conditions.



Fig. 10 Calculated half-life (t1/2) for the oxidation of 2-TBI by metal complexes at different experimental conditions.



Fig. 11 2-TBI removal by the metal complexes at different experimental conditions.

3.6. Mechanism of photocatalysed degradation of 2-TBI

2-TBI oxidation products were analysed by HPLC-MS technique to propose a mechanism for its degradation. Figure 12 shows HPLC-MS chromatogram with three different fragments obtained from the degradation of 2-TBI.

3

9 10

11

<u>ģ</u>6

2020 Downloaded by 7 C C C C C C

Bublished on 2 Leouary

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60 Journal Name



Fig. 12 Combined HPLC-MS chromatogram of the degradation of 2-TBI.



Fig. 13 Rout of the fragmentation of 2-TBI.

The degraded products I, II and III with their corresponding m/z, 119, 135, and 136 respectively (Fig. 12) were characterized by MS spectra. In addition, 1H NMR (400 MHz) spectra (Fig.S5) for 2-TBI was analysed before and after the catalysed oxidation; the aromatic and aliphatic region of the oxidized products were identified. According to the results obtained from the analyses of degraded products, a possible degradation rout (Fig. 13) for 2-TBI, and its oxidation mechanism (Fig. 14) was proposed considering the presence of metal complex catalyst and visible light irradiation. Under the visible light irradiation, excitation of electron (e⁻) from the valence band (VB) of metal ion to the conduction band (CB) leaving behind a hole (h⁺) in VB (Eqn. 1) takes place (Eqn. 3). This photo-generated electron in excited state of the metal complex interact with hydrogen peroxide to generate hydroxyl radicals that involve in the 2-TBI oxidation.

 $[CoQ3] + light \rightarrow [CoQ3] (h^+ + e^-)$ (3)





(4) View Article Online DOI: 10.1039/C9NJ04027G

Fig. 14 Proposed mechanism for 2-TBI oxidation by 'OH radicals.

3.7. DFT calculations

To unveil the mechanism of hydroxyl radical formation from H2O2 in the presence of metal complex catalysts, and also to simulate the electron migration from metallic centre to hydrogen peroxide, molecular energy calculations by DFT were performed. In the first step, to understand the ground state nature, molecular optimization of the metal complexes $[M^{3+}(L-1)_3]$ (M=Cr³⁺, Fe³⁺, Co³⁺) was carried out in ground state using an unrestricted uB3LYP functional with LANL2DZ basis set in an aqueous medium through an IEF-PCM model. With the collected information from ground state (S₀), its excitation process was studied via unrestricted TD-DFT calculations. Since its application as visible light photocatalysts is being studied, it is important to know the behaviour of these molecules upon excitation by low energy photons, γ (6.0≥E γ ≥1.54 eV) present in visible light. As the visible light limits the higher energy

Journal Name

ARTICLE

1 2

3

4

5

6

7

8

9

10

11

12

13 194 195

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

excitations, excitation process from ground state (S_0) to the first excited state ($S_0 \rightarrow S_1$) was analysed. To determine the *sp* and *d* orbital hybridization in metal complexes, different multiplicity have been previously executed since the individual electron transfer reactions depend strongly on the spin and energy state of the electrons. Since during the excitation process, unpaired electrons may be easily excited because paired electrons are intrinsically bound to its orbital; nevertheless, excitation of single electrons could undergo rapid relaxation processes included photon emission, electron injection and electron transfer are dependent on energetic limitations.



Fig. 15 Frontier Molecular Energies for HQ complexes.

As can be inferred from figure 15, the energy gap (Δ EHOMO-LUMO) observed among the studied complexes was, $\Delta E=3.17$ eV for CoQ3; ΔE =3.7 eV for FeQ3 and finally ΔE =3.0 eV for CrQ3. In order to explain a little controversy observed between the HOMO-LUMO energy where the lower value of band gap lies in CrQ3 and the experimental results where CoQ3 showed a higher oxidization rate, spin coupling and Density of States (DOS) of the catalysts were analysed. From the electronic configuration (Fig. S6) it is clear that Cr³⁺ and Fe^{3+} complexes are in a doublet state with only one α electron (+1/2) which would leave an empty HOMO during the excitation process, which is thermodynamically viable; however, resulting excited state would not be stable and thus rather undergo vibrational relaxation (Fig. 16). On the other hand, for CoQ3, a singlet configuration is observed; after light absorption, single electronic excitation is observed (Fig. 16) which would result in a triplet state with a change of spin polarization from $\alpha \rightarrow \beta$ (-1/2). This configuration is fairly stable that endures an intermolecular electronic transfer from complex to hydrogen peroxide (Scheme 1).



Scheme 1 Spin dependent 'OH radical formation.



Fig. 16 Density of states (DOS) plot for the metal complexes of 8-HQ.

The viability of the electron migration pathway, transition state (TS) within the electron transfer process between the metallic centre and H₂O₂ in order to form hydroxyl radicals was determined, and optimized by QST3 approach (Fig. 17). In addition, thermodynamic feasibility of the interaction of metal complex with H_2O_2 was analysed through intrinsic reaction coordinates (IRC) parameters such as a activation energy (E_a), transition states (TS) and free energy (ΔE) that were determined using a uBB1K/LANL2DZ basis set in a full aqueous media given by a IEF-PCM model. Based on the experimental evidence, the formation of •OH radicals is triggered and depends on light irradiation (Scheme 2). For explaining this behaviour, a mechanism has been proposed based on the excitation of the complex followed by a multistep relaxation (Eqns. 5-7) that allows the final formation of two •OH radicals through a single electron transfer process (SET), and also permits regeneration of metallic complex catalyst (Eqn. 7)

 $[M3+(L-1)_3] + \gamma [M^{3+}(L^{-1})_3] + \gamma \rightarrow ([M^{3+}(L^{-1})_3])_t^* \quad (Phase 1) \quad (5)$

3

4

5

6

7

8

9

10

11

12

13

ģ]6

> 46

47

48

49

50 51

52

53

54 55

56 57 58

59

60

(8)

Journal Name

$$([M^{3+}(L^{-1})_{3}])_{t}^{*} + H_{2}O_{2} \rightarrow ([M^{4+}(L^{-1})_{3}]^{+})_{s}^{\bullet} + ^{\bullet}OH + ^{\bullet}OH$$
(Phase 2) (6)
$$([M^{4+}(L^{-1})_{3}]^{+})_{s}^{\bullet} + ^{\bullet}OH \rightarrow ([M^{3+}(L^{-1})_{3}]) + ^{\bullet}OH$$
(Phase 3) (7)
Global:

$$[M^{3+}(L^{-1})_3] + H_2O_2 + \gamma \rightarrow [M^{3+}(L^{-1})_3] + 2^{\bullet}OH$$

According to this proposal, a low energy-visible light photon (γ) collides with $[M^{3+}(L^{-1})_3]$ complex which will excite one of its electrons from basal (S₀) to its first excited state (S₁).



Scheme 2 Radical Oxygen Species production (ROS) from H_2O_2 by photoexcitation of $[M^{3+}(L^{-1})_3]$.

Thermodynamic parameters for the metal complex catalysed generation of 'OH radicals from H_2O_2 are shown in table 6. It can be observed that the energy needed for the formation and deformation of the adduct between **CoQ3** and H_2O_2 is lower than the other studied catalysts, which agrees with the experimentally obtained kinetic data.

Table 6 Thermodynamic parameters for electron transfer for'OH formation by 8-HQ complexes.

	Total	ΔE (kcal/mol)					
System	(10 ⁻⁶ kcal/mol)	(M ³⁺ L ⁻ ₃)*+H ₂ O ₂	TS1	(M ³⁺ L ⁻ ₃)•+ ⁻ OH+•OH	TS2	(M ³⁺ L ⁻ ₃)+•OH	
$[Cr^{3+}L_{3}]+H_{2}O_{2}$	-1.05	37.58	35.88	26.56	31.1	16.65	
$[Fe^{3+}L_{3}]+H_{2}O_{2}$	-1.07	64.93	60.21	49.89	54.65	41.09	
$[Co^{3+}L_{3}]+H_{2}O_{2}$	-1.09	70.76	64.4	54.38	59.36	45.93	



Fig. 17 IRC profile for 'OH radical formation by different metal complexes.

As can be observed in figure 17, excitation energies for the studied complexes vary from low energy: excitation process (E=32.58 kcal/mol) for the case of CoQ3 to high energy for the case of FeQ3 (E=64.93 kcal/mol) and CrQ3 (E=70.86 kcal/mol). Interestingly there are no important changes in the energy of formation after the excitation process was observed among the studied complexes, indicating that the crucial step is the light-induced excitation process, which has also been demonstrated experimentally observing increased rate of 2-TBI degradation under visible light irradiation.

In addition, to recognize the processes that lead to the degradation of 2-TBI and their corresponding degradation intermediate products, intrinsic reaction coordinates (IRC) parameters such as a activation energy (E_a), transition states (TS), and free energy (ΔE) were determined using a uBB95K/6-311G(d,p) basis set in aqueous media. Figures 18 and 19 show computationally determined thermodynamical parameters including solvent effects for the above-proposed mechanism in figure 14 for 2-TBI degradation. The negative value of ΔE (-7.8 kcal/mol) observed for step 1 indicates that the interaction of OH radicals with sulphur atom of the thiol group in 2-TBI (Fig. 14) is thermodynamically feasible. Step 1 is followed by a gradual decrease of ΔE up to the formation of stable intermediate in step 4 through which the sulfuric acid formed as a by-product is eliminated. In step 5, OH radical bonds with N atom of the imidazole ring breaking the π bond in C=N, and this process is followed by few fast steps up to the formation of stable intermediates in steps 11 and 12. The most stable intermediate formed in 2-TBI degradation process is found in step 16 since the activation energy (E_a) needed for this intermediate to follow the next step 17 is maximum ΔE (-155.7 kcal/mol). As can be seen in steps 18 and 19, there is no higher energy process has observed after step 17, indicates that the final product formed in the degradation of 2-TB can be considered in step 17. By relating this IRC profile with the experimentally obtained 2-TBI degraded products by HPLC-MS, it can be concluded that the peaks I, II and III in figure 12 are corresponding to the stable by-products observed in steps 11, 12 and 16 respectively.

This journal is © The Royal Society of Chemistry 20xx

/ Accepted Manu

Journal Name





Fig. 18 Thermodynamic parameters for the oxidation of 2-TBI by hydroxyl radicals a) Activation energies (E_a); b) Free energy (ΔE) profile.

This observation is affirmed by the internal reaction profile (IRC) (Fig. 19) that performed for the oxidation of 2-TBI by OH radicals using uB3LYP/BB1K in aqueous media. A gradual decrease in the activation energy for each transition state (TS) observed in figure 18 confirms the thermodynamic feasibility of the proposed degradation mechanism in figure 14.



Fig. 19 Internal Reaction profile for the oxidation of 2-TBI by 'OH radicals obtained by uB3LYP/BB1K in aqueous system.

Conclusions

Metal complexes of Cr³⁺, Co³⁺, and Fe³⁺ with 8hydroxyquinoline were synthesized and characterized by different analytical techniques revealing 1:3 metal to ligand stoichiometry for the complex formation by an octahedral

geometry along with an ethanol molecule bonded with one of the oxygen atoms of 8-quinolinolato aniorothrough/asydrogen bond. The catalytic activity of synthesized metal complexes was investigated over the oxidation of 2-TBI with H₂O₂ by UVvis spectroscopy at different experimental conditions. Among the all studied catalysts, CoQ3 showed a better catalytic activity towards 2-TBI removal with 99.1% under the visible light irradiation at neutral pH. The experimental results were corroborated with theoretically obtained energy components comprising in the activation energy of 2-TBI degradation pathway. It was found that the activation energy involved for the formation of hydroxyl radical from H_2O_2 that is responsible for 2-TBI oxidation is diminished with CoQ3 due to the increased photo-excited electron transfer favoured by lower transition state energy of the adduct **CoQ3**-H₂O₂. In addition, a thermodynamically feasible mechanism for 2-TBI degradation is proposed according to the experimental results, and analysed by DFT.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors acknowledge PRODEP (Programa para el Desarrollo Profesional Docente en Educación Superior, DSA/103.5/15/14210), Mexico, for financial support through the programe "Red Temática de Colaboración Academica-2015". Also acknowledge DGTIC-UNAM (Dirección General de Cómputo y de Tecnologías de Información y Comunicación, Universidad Nacional Autónoma de México) for the computational facilities and USAI (Unidad de Servicios de Apoyo a la Investigación, Facultad de Química, UNAM) for analytical services.

References

- 1 D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Springer Science+Business Media, LLC, New York, 1994.
- W. P. Kwan and B. M. Voelker, *Environ. Sci. Technol.*, 2003, 37, 1150-1158.
- 3 J. J. Pignatello, E. Oliveros and A. MacKay, *Crit. Rev. Env. Sci. Tec.*, 2006, **36**, 1-84.
- 4 K. C. Gupta and A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420-1450.
- 5 X. T. Zhou, H. B. Ji and S. G. Liu, *Tetrahedron Lett.*, 2013, **54**, 3882-3885.
- 6 V. Corce, L. M. Chamoreau, E. Derat, J. P. Goddard, C. Ollivier and L. Fensterbank, *Angew. Chem.*, Int. Ed. Engl, 2015, **54**, 11414-11418.
- Á. Gutiérrez-Bonet, J. C. Tellis, J. K. Matsui, B. A. Vara and G.
 A. Molander, ACS Cat., 2016, 6, 8004-8008.
- 8 G. Czapski, A. Samuni and D. Meisel, J. Phys. Chem., 1971, 75, 3271-3280.
- 9 S. A. Weitzman and P. Graceffa, Arch. Biochem. Biophys., 1984, 228, 373-376.
- 10 C. M. Miller and R. L. Valentine, Water Res., 1995, 29, 2353-2359.

This journal is © The Royal Society of Chemistry 20xx

3

4

5

6

7

8

9

10

11

12

13

ģ]6

5:60007/E2/

KARRABEUNIVERSUTKONS/

<u>\$</u>9

2020 Downbade 2020 Downbade

42

43

44

45

46

47

49

50

51

52

53

54

55

56

57

Journal Name

- 11 R. L. Valentine and H. C. Ann Wang, Iron Oxide Surface Catalyzed Oxidation of Quinoline by Hydrogen Peroxide, J. Environ. Eng., 1998, 124, 31-38.
- 12 H. Lu, Z. Zhu, H. Zhang, J. Zhu, Y. Qiu, L. Zhu and S. Küppers, ACS Appl. Mater. Inter., 2016, 8, 25343-25352.
- 13 C. Catrinescu, C. Teodosiu, M. Macoveanu, J. Miehe-Brendle and R. Le Dred, Water Res., 2003, 37, 1154-1160.
- 14 E. G. Garrido-Ramírez, B. K. G. Theng and M. L. Mora, Appl. Clay Sci., 2010, 47, 182-192.
- 15 A. Bokare and W. Choi, Review of iron-free Fenton-like systems for activating H2O2 in advanced oxidation processes, 2014, J. Hazard. Mater., 30, 275:121-35.
- 16 N. Wang, T. Zheng, G. Zhang and P. Wang, J. Environ. Chem. Eng., 2016, 4, 762-787.
- 17 G. Lyngsie, L. Krumina, A. Tunlid and P. Persson, Sci. Rep., 2018, 8, 10834.
- 18 D. Wang and D. Astruc, Chem. Soc. Rev., 2017, 46, 816-854.
- 19 C. Merli, E. Petrucci, A. Da Pozzo and M. Pernetti, Ann. Chim., 2003, **93**, 761-770.
- 20 A. Babuponnusami and K. Muthukumar, J. Environ. Chem. Eng., 2014, 2, 557-572.
- 21 L.-Z. Tang, C.-N. Lin and S.-Z. Zhan, Trans. Met. Chem., 2016, **41**, 819-825.
- 22 A. M. Jones, P. J. Griffin, R. N. Collins and T. D. Waite, Geochim. Cosmochim. Acta, 2014, 145, 1-12.
- 23 A. B. Getsoian, Z. Zhai and A. T. Bell, J. A. Chem. Soc., 2014, 136, 13684-13697.
- 24 S. Ghosh, N. A. Kouame, L. Ramos, S. Remita, A. Dazzi, A. Deniset-Besseau, P. Beaunier, F. Goubard, P. H. Aubert and H. Remita, Nat Mater., 2015, 14, 505-511.
- 25 C. Wu, A. De Visscher and I. D. Gates, RSC Adv., 2017, 7, 35776-35785.
- 26 L. Wang, I. Rörich, C. Ramanan, P. W. M. Blom, W. Huang, R. Li and K. A. I. Zhang, Cat. Sci. Technol., 2018, 8, 3539-3547.
- 27 N. Kaur, Komal, S. Gupta, V. Kumar, K. B. Tikoo, S. Singhal and N. Goel, N. J. Chem., 2019, 43, 1505-1516.
- 28 J. Tao, M. Yang, J. W. Chai, J. S. Pan, Y. P. Feng and S. J. Wang, J. Phys. Chem. C, 2014, 118, 994-1000.
- 29 M. H. Habibi, S. Tangestaninejad and B. Yadollahi, Appl. Cat. B: Environ., 2001, 33, 57-63.
- 30 A. S. Aprem, K. Joseph, T. Mathew, V. Altstaedt and S. Thomas, Eur. Polym. J., 2003, 39, 1451-1460.
- 31 B. RCI, Toxicological evaluation of 2-Mercaptobenzimidazole, Germany, 2010, 218, 8-37.
- 32 B. Rodgers and W. Waddell, The Science and Technology of Rubber (Fourth Edition), Academic Press, Boston, 2013, 417-471.
- 33 I. B. Obot, Z. M. Gasem and S. A. Umoren, Int. J. Electrochem. Sci., 2014, 9, 2367-2378.
- 34 R. C. C. a. J. S. Reid, Acta Cryst. A, 1995, 51, 887--897.
- 35 G. Sheldrick, Acta Cryst. A, 2015, 71, 3-8.
- 36 G. Sheldrick, Acta Cryst. C, 2015, 71, 3-8.
- 37 L. Farrugia, J. Appl. Cryst., 1999, 32, 837-838.
- 38 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. 48 Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. 58 Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L.
- 59 60

Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Gaussian Inc, Wallingford, CT 2016 039/C9NJ04027G

- 39 H. J. Guadalupe, J. Narayanan and T. Pandiyan, J. Mol. Struct., 2011, 989, 70-79.
- 40 W. P. Ozimiński and J. C. Dobrowolski, J. Phys. Org. Chem., 2009, 22, 769-778.
- 41 A. D. Becke, J. Chem. Phys., 1996, 104, 1040-1046.
- 42 J. Narayanan, A. H. Carlos-Alberto, L. M. Arturo, H. Höpfl, V. C. Enrique-Fernando, R. A. Fernando, W. K. Fernando-Toyohiko, J. E. Velazquez-Lopez and A. O. Lesli, J. Mol. Struct., 2018, 1155, 831-842.
- 43 D. Avcı, S. Altürk, Ö. Tamer, M. Kuşbazoğlu and Y. Atalay, J. Mol. Struct., 2017, 1143, 116-126.
- 44 A. Teimouri, A. N. Chermahini, K. Taban and H. A. Dabbagh, Spectrochim. A Mol. Bio. Spectros., 2009, 72, 369-377.
- 45 C. Engelter, C. L. Knight and D. A. Thornton, Spectros. Lett., 1989, **22**, 1161-1172.
- 46 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th Ed., J. Wiley and Sons, New York, 1997.
- 47 S. Shanmuga Sundara Raj, I. A. Razak, H.-K. Fun, P.-S. Zhao, F. Jian, X. Yang, L. Lu and X. Wang, Acta Cryst. C, 2000, 56, e130-e131.
- 48 P. Basu and A. Chakravorty, J. Chem. Soc. Chem. Comm., 1992, 809-810.
- 49 R.-G. Xiong, X.-Z. You, Q.-J. Wu and X.-Y. Huang, Acta Cryst. C, 1995, 51, 1978-1980.
- 50 Y. J. Wang, Z. H. Fu, X. Wen, C. Y. Rong, W. F. Wu, C. Zhang, J. Deng, B. H. Dai, S. R. Kirk and D. L. Yin, J. Mol. Cat. A: Chem., 2014, 383, 46-52.
- 51 Y. Wang, X. Wen, C. Rong, S. Tang, W. Wu, C. Zhang, Y. Liu and Z. Fu, J. Mol. Cat. A: Chem., 2016, 411, 103-109.
- 52 Y. Y. Wang, Y. Ren, J. Liu, C. Q. Zhang, S. Q. Xia and X. T. Tao, Dyes Piqm., 2016, 133, 9-15.
- 53 H.-R. Zhang, K.-B. Huang, Z.-F. Chen, Y.-C. Liu, Y.-N. Liu, T. Meng, Q.-P. Qin, B.-Q. Zou and H. Liang, Med. Chem. Comm., 2016, 7, 806-812.
- 54 J. F. X. J. Zhang Shusheng, Ind. J. Chem., 2002, 41A, 1199-1201.
- 55 J. S. Griffith, The Theory of Transition Metal Ions, Cambridge University Press, Cambridge, 1964.
- 56 R. L. Carlin, Transition Metal Chemistry, Editorial Marcel-Dekker, Vol.4, 1968.
- 57 A. B. P. Lever, Inorganic electronic spectroscopy, Elsevier Science Publishers Company, Inc., New York, 1984.
- 58 E. W. A. F. Holleman, N. Wiberg, M. Eagleson and W. Brewer, Inorganic Chemistry, Academic Press, New York, 2001.
- 59 M. E. Malefane, U. Feleni and A. T. Kuvarega, N. J. Chem., 2019, 43, 11348-11362.

