

FULL PAPER



Study molecular modeling and the effect of some biological metals on the efficiency of norfloxacin in presence of 3-(bromoacetyl)coumarin

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Abstract

A series of new mixed ligand metal complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized by the reaction of norfloxacin (NOR) with 3-(bromoacetyl)coumarin (BAC) in 1:1:1 (Mⁿ⁺:NOR:BAC) molar ratio, which characterized by elemental analysis, spectroscopic measurements (FT-IR, UV-Vis) molar conductance, effective magnetic moments, and thermogravimetric analysis (TG) and (DTG). All the complexes soluble in DMSO and the conductivity measurement indicate that the complexes are electrolyte with ratio 1:1 for Mn(II), Fe(II), and Zn(II) and 1:2 for Co(II), Ni(II), and Cu(II). Electronic and magnetic data elucidated the octahedral structure for all complexes. Assorted thermodynamic factors are calculated, and the results are explicated. Molecular modeling calculations (bond angles, dihedral angles, total energy, heat of formation, and dipole moment) confirm the structural geometry of the complexes and indicate the very good agreement between the computed and experimental geometrical parameters. The calculated data for the hardness (η) and absolute softness (σ) showed that all complexes are soft with respect to ligands. The two ligands and their metal complexes have also been screened for their antibacterial and antifungal activity against some selected species; the data showed that the complexes have remarkable potency as compared with the parent ligands.

KEYWORDS

3-(bromoacetyl)coumarin DFT, antimicrobial activity, mixed ligand complexes, norfloxacin

1 | INTRODUCTION

Fluoroquinolone is an important antibiotic family; they are particularly interesting for application due to their ability to chelate with metal ions. In general, it is active against a wide variety of aerobic gram-negative and gram-positive bacteria specifically and active against aminoglycoside-resistant, *Pseudomonas aeruginosa* and betalactamase producing organisms,^[1–4] consequently, much research concerning the complexation of fluoroquinolone with different metal ions has been discussed in the literature.^[5–8] The crystal structures of several free fluoroquinolone molecules indicate that in some cases, the carboxylic group is protonated and the molecule thus exists in a zwitterionic form with protonated terminal nitrogen of the piperazine ring, or in other cases, the carboxylic group is deprotonated, and the hydrogen atom of this group is hydrogen bonded to an adjacent 4-oxo atom in a solid state.^[9] Fluoroquinolones behaved as bidentate ligands through one oxygen of carboxylic group and oxygen of pyridon group.^[10] In the literature survey, fluoroquinolones may be coordinated with metal ions as monodentate through only one nitrogen of piperazine ring or as a bridging ligand between two metal ions.^[9,11-14] NOR (Scheme 1A) is a one of second generation synthetic fluoroquinolone with a broad-spectrum antibacterial agent for oral administration. The coordination chemistry of NOR with metal ions of biological and pharmaceutical importance is considerable interest.^[15,16] The NOR interacted with metal particles for formalization complexes interact accordingly a bidentate through the oxygen atoms of carboxylic and pyridon groups.^[17-19]

Coumarin is the parent component of a family of numerous compounds found in a wide range of natural products. It is thought that coumarin's antibacterial action comes from either killing or inhibiting the microbe's active site.^[20] Coumarin compounds have been shown to produce a wide range of metal chelates with various chelated modes, spectroscopic characteristics, and possible uses. The complexation of coumarin-derived ligands with different transition metals, in particular, has been identified as a viable path to the creation of novel medicinal medicines. A number of coumarin derivatives and transition complexes were previously produced. The coordination capabilities and complexation behaviors of liable ligands need to be investigated more. Coumarin exists in a number of forms due to the numerous substitutions that may be made to their basic framework, which influence their bioactivity.^[21-23] 3-(Bromoacetyl)coumarin (BAC) (Scheme 1B) is a coumarin counterpart with the substitute bromoacetyl in position 3. It is well known that the existence of a metal ion bonded to biologically active materials may enhance their activity by changing electronic and geometrical structure. The goal of this research is to synthesize and investigate the influence of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions on the antibacterial efficiency of NOR in the presence of BAC. In order to evaluate the binding of the new mixed ligand complexes, the magnetic, spectral, and thermal methods were used. Density functional theory (DFT) was used to quantify the cation type impact on conceptual of the chelates and predict their minimized architecture, as well as the total energy, heat of formation, and total dipole moment. Indeed, the antimicrobial activity of ligands and their metal complexes were screened against selected kind of pathogenic bacteria and fungi.

2 | EXPERIMENTAL

2.1 | Materials and instruments



Whole chemicals utilized were of analytical reagent grade and applied with no additional purifying. ZnSO₄

SCHEME 1 (A) 1-Ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid and its zwitterion and (B) 2-bromo-1-(2-methylene-2*H*-chromen-3-yl)ethanone

(99.90%), CuCl₂.2H₂O (99.90%), NiCl₂.6H₂O (99.90%), CoCl₂.6 H₂O (99.90%), FeSO₄ (99.90%), and MnSO₄.6H₂O (99.90%) were obtained from Aldrich Chemical Co. While NOR was obtained from Merck Chemical Co. BAC, acetone, DMSO, AgNO₃, BaCl₂, K₂CrO₄, and NaOH were purchased from Fluka Chemical Co. Table S1 lists all of the instruments that were utilized.

2.2 | Synthesis of mixed ligand complexes

The buff [Mn (NOR)(BAC)(H₂O)₂]SO₄.2H₂O complex, (1), was prepared by blending 1 mmol (0.26 g) of MnSO₄.6H₂O with 20-ml acetone drop by drop into an agitated suspending mixture 1 mmol (0.27 g) of BAC in 1-mmol (0.32 g) NOR with 50-ml acetone. The mixture was refluxed for 6 h before being drained and dried in vacuo. The brown, light brown, faint green, light green, and pale brown solid complexes [Fe (NOR)(BAC)(H₂O)₂] SO₄.2H₂O (2), [Co (NOR)(BAC)(H₂O)₂]Cl₂.2H₂O (3), [Ni (NOR)(BAC)(H₂O)₂]Cl₂.2H₂O (4), [Cu (NOR)(BAC) (H₂O)₂]Cl₂ (5), and [Zn (NOR)(BAC)(H₂O)₂]SO₄.2H₂O (6) were set in identical technique qualified above by utilizing FeSO₄, CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, and ZnSO₄, respectively.

2.3 | Antimicrobial investigation

2.3.1 | Tested bacteria and fungi

The tested bacterial strains were *Staphylococcus aureus* (*S. aureus*), *Listeria monocytogens* (*L. monocytogens*), *Bacillus cereus* (*B. cereus*), and *Acnietobacter baumanii* (*A. bauamanii*). The tested phytopathogenic fungi were *Aspergillums niger* (*A. niger*), *Aspergillums terreus* (*A. terreus*), *Candida albicans* (*C. albicans*), and *Fusarium oxysporium* (*F. oxysporium*). All tested strains have been conserved as pure cultures in the collection of the microbiological laboratory, at Faculty of Science, Zagazig University, Egypt.

2.3.2 | Bactericidal and fungicidal evaluation

The disc diffusion technique has been used.^[24] Each isolate was suspended in sterilized Millipore water, after that put into Müller-Hinton agar medium (MHA) (0.2 g/L beef extract, 17.5 g/L acid hydro lysate of casein, 1.5 g/L starch and 17 g/L agar) (0.7%) for bacteria and Czapex-Dox agar medium (30 g/L sucrose, 3 g/L NaNo₃, 1 g/L K₂HPO₄, 0.5 KCL, 0.01 FeSO₄, and 20 g/L agar) for fungi. After autoclaved, it cooled to 47°C and then seeded with tested microorganisms. After solidification prepare disks were used approximately 6 mm in diameter and placed in a petri dish, and 5-mm diameter holes were punched by borer sterile cork-borer. The investigated compounds were dissolved in DMSO (1×10^{-3} M). Ciprofloxacin and moxifloxacin were utilized as standard material. The antimicrobial effect was determined after 24 h at 37°C for bacteria and 7 days at 30°C for fungi, by measuring the diameter of inhibition zones (mm). The experiment was carried out in triplicate with ±SDs.

3 | RESULTS AND DISCUSSION

NOR interacts with manganese (II), iron (II), cobalt (II), nickel (II), copper (II), and zinc (II) ions, respectively, in the existence of BAC to form a variety of complexes (1). (2), (3), (4), (5), and (6). On the premise of its elemental analysis, the complexes' stoichiometry was determined (Table 1). The complexes' formulae and architecture were determined using physical and chemical characteristics such as magnetic properties, melting points, molar conductance, and spectral measurement. The results of analytical data indicate that all the complexes contain water molecules and the number of bound water molecules in these complexes being different. The molar conductivity for freshly prepared DMF solutions $(1 \times 10^{-3} \text{ M})$ of the complexes was measured at room temperature. The data show the molar conductance value of the complexes (1). (2), and (6) with sulphate as counter ions found around 142.00 S cm² mol⁻¹ indicating these complexes as 1:1 electrolytes, while the complexes (3), (4), and (5) with Cl⁻ counter ions with molar conductance value nearly around 122.00 S cm² mol⁻¹ are 1:2 electrolytes.^[25] The results are consistent with qualitative studies that indicated the existence of chloride and sulphate anions as counter ions.^[26] At ambient temperature, the magnetic properties (as B.M) were recorded, revealing that all of chelates are paramagnetic, with the exception of complex (6), which has diamagnetic properties, and that all of them had octahedral.^[27,28]

3.1 | FT-IR data and bonding

The significant IR spectral data of NOR, BAC, and their metal complexes were listed in Table 2 lists and showed in Figure S1. The main bands were discussed in order to determine the site and kind of coordination that may be involved in chelation from ligands to metal ions. The NOR spectrum has two peaks at 1736 and 1619 cm⁻¹ that are attributed to ν (C=O)_{COOH} and ν (C=O)_{pyr},

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TABLE 1

Compounds molecular				Found (Calcd	.) (%)						V
and empirical formulae	Yield%	$Mp/^{o}C$	Color	C	Н	Z	М	cı	S	$\mu_{eff}\left(B.M\right)$	$S \text{ cm}^2 \text{ mol}^{-1}$
NOR 319.331 (C ₁₆ H ₁₈ N ₃ O ₃ F)	ı	230	Buff	60.00 (60.13)	5.59 (5.64)	13.10 (13.15)			ı		0
BAC 266.9 (C ₁₁ H ₇ O ₃ Br)	ı	164	Pale yellow	49.30 (49.45)	2.55 (2.62)						4.79
(1) 808.74 (MnC ₂₇ H ₃₃ N ₃ O ₁₄ FBrS)	90.06	300	Buff	39.95 (40.06)	4.00 (4.08)	5.11 (5.19)	6.71 (6.79)		3.89 (3.95)	5.36	142.67
(2) 773.65 (FeC ₂₇ H ₂₉ N ₃ O ₁₂ FBrS)	98.9	180	Brown	41.79 (41.87)	3.67 (3.74)	5.36 (5.42)	7.16 (7.21)		4.04 (4.13)	4.90	140.50
(3) 805.73 (CoC ₂₇ H ₃₅ N ₃ O ₁₁ FBrCl ₂)	98.7	200	Light brown	40.10 (40.22)	4.22 (4.34)	5.11 (5.21)	7.25 (7.31)	8.73 (8.81)		3.89	120.23
(4) 805.49 (NiC ₂₇ H ₃₅ N ₃ O ₁₁ FBrCl ₂)	95.1	200	Faint green	40.11 (40.22)	4.27 (4.35)	5.13 (5.21)	7.20 (7.29)	8.72 (8.81)		3.21	122.00
(5) 792.34 (CuC ₂₇ H ₃₃ N ₃ O ₁₀ FBrCl ₂)	94.7	190	Light green	40.73 (40.89)	4.09 (4.16)	5.20 (5.30)	7.92 (8.01)	8.90 (8.96)		1.74	125.50
(6) 819.21 (ZnC ₂₇ H ₃₃ N ₃ O ₁₄ FBrS)	99.1	280	Pale brown	39.42 (39.55)	3.96 (4.02)	5.05 (5.12)	7.90 (7.98)	,	3.82 (3.90)		144.52

Compounds	ν(Ο-Η); H ₂ O; COOH	v(C=O) _{lactone}	$\nu(C=O)_{lpha,eta}$ unsaturated	ν(C=0) _{COOH}	ν _{as} (COO ⁻)	ν(C=0) _{pyr}	ν _s (COO ⁻)	ν(M-0)
Nor	3425w	-	-	1736vs	-	1619vs	-	-
BAC	-	1729vs	1674s	-	-	-	-	-
(1)	3372mbr	1736s	1605 m	-	1678 m	1547s	1419 m	605 m, 555 m, 513w, 463w
(2)	3417mbr	1736s	1632s	-	1674 m	1551 m	1408 m	670 m, 617w, 513 m
(3)	3426sbr	1736s	1624s	-	1674s	1551 m	1404 m	664w, 629w, 513w
(4)	3410mbr	1736s	1612 m	-	1674 m	1547w	1408 m	633vw, 555 m, 509w
(5)	3441mbr	1736s	1631s	-	1674s	1581 m	1408 m	629w, 601w, 517 m
(6)	3422mbr	1734 ms	1624 m	-	1670w	1550w	1410w	621 m, 555vw, 505vw

TABLE 2 Selected infrared absorption frequencies (cm⁻¹) of NOR, BAC, and their metal complexes

Abbreviations: s, strong; w, weak; m, medium; br, broad; v, stretching; v, very.

respectively.^[16-18] The ν (C=O)COOH peak at 1736 cm⁻¹ disappeared in the spectra of the complexes. Two very strong bands are present around 1674 cm^{-1} and 1415 cm⁻¹ assigned to (COO-) asymmetric and symmetric stretches, respectively, with an average Δv around 259 cm⁻¹, indicating a monodentate coordination of carboxylate group.^[29,30] The shift of the peak assigned to pyridone group (1619 cm^{-1}) to lower value around 1555 cm^{-1} indicates that the oxygen of pyridone group is coordinated to the metal ions.^[31] The BAC spectrum has two distinct peaks that have been ascribed to $\nu(C=O)_{\alpha}$. _{β-unsaturated} and ν (C=O)_{lactone} at 1674 and 1729 cm⁻¹, respectively.^[32] In the IR spectra of the complexes, the band corresponding to the ν (C=O)_{α , β -unsaturated} shifted to lower frequency, which indicate the participation of the oxygen moiety's of α , β -unsaturated ketone with the metal ions. Also, the band of $\nu(C=O)_{lactone}$ is shifted to higher values in all complexes (Table 2), which is a good indication that the inclusion of lactone carbonyl oxygen atom of coumarin in chelation with metal ions.^[32,33] The broad band at 3420 cm⁻¹ showed the vibrational mode of ν (O–H), due to the presence of lattice water. The appearance of bands around 3350, 840, and 600 cm^{-1} in the spectra of all complexes were attributed to ν (O-H), rocking and wagging vibration of the coordinated water.^[34] The presence of new peaks with different intensities which characteristics for ν (M–O) were observed at 605, 555, 513, and 463 cm^{-1} for Mn(II), 670, 617, and 513 cm^{-1} for Fe(II), 664, 629, and 513 cm^{-1} for Co(II), 633, 555, and 509 cm^{-1} for Ni(II), 629, 601, and 517 cm^{-1} for Cu(II), and 621, 555, and 505 cm^{-1} for Zn(II). The proposed structures for complexes are shown in Figure 1.

3.2 | Electronic spectra and magnetic moments

The assignments of the spotted electronic absorption bands of the NOR, BAC, and their metal complexes were listed in Table 3. In fact, the electronic spectrum of NOR exhibit various peaks at 305 and 340, 370 nm, and BAC exhibits peaks at 305 and 335, 370 nm (Figure S2) that may be referred to $\pi - \pi^*$ and $n - \pi^*$ transitions, respectively.^[32,35] The shift of the absorption bands to higher values (bathochromic shift) and to lower values (hypsochromic shift) and presence of new bands in the spectra of complexes indicate that the formation of their metal complexes. In addition, the existence of new peaks in the range 505-515 nm that can be ascribed to ligandmetal charge transfer^[36-38] and the development of new bands in the range 610-645 nm in all complexes except complex (6) can be ascribed to d-d transition.^[39-42] The absorbance spectrum of complex (1) (with magnetic 5.36 B.M.) showed two identified bands at 610 and 645 nm, which may be assigned to ${}^{6}A_{1} \rightarrow {}^{4}T_{2}(G)$ and ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}({}^{4}G)$ transition, respectively.^[43] The absorption peak at 625 nm in complex (2) spectrum with the magnetic moment (4.90 B.M.) can be attributed to ${}^{5}T_{2g}$ (D)- ${}^{5}E_{g}$ transition.^[28,44] Complex (3) absorption spectrum exhibited peak at 620 nm which may be ascribed to ${}^{4}T_{1\sigma}$ $(F) \rightarrow {}^{4}T_{1g}$ (P) transition in support of octahedral shape with magnetic moment (3.89 B.M.).^[45] The complex (4) showed absorption peak at 615 nm, which may be assigned to ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ transition and supporting distorted octahedral geometry.^[28] The peak observed at 630 nm for complex (5) may be assigned to ${}^{2}B_{1g} \rightarrow {}^{2}E_{1g}$

FIGURE 1 The coordination mode of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with NOR and BAC

2+



TABLE 3 UV-Vis spectra of NOR, BAC, and their metal complexes

			Mixed ligand complex with						
Assignments (nm)	NOR	BAC	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	
$\pi - \pi^*$ transitions	305	305	300	295	295	300	295	295	
$n-\pi^*$ transitions	340, 370	335, 370	325, 370	335, 410	330, 370	325, 370	335, 385	335, 370	
Ligand-metal charge transfer	-	-	515	515	505	515	515	510	
d-d transition	-	-	610, 645	625	620	615	630	-	

transition with the magnetic moment (1.74 B.M.) is very close to spin value (1.73 B.M.) expected for an octahedral geometry.^[33,46]

3.3 | Thermogravimetric analyses

Thermal studies were used to investigate the chemical composition of the resulting volatile decomposing constituents and the characteristics of the complexes. The majority of compounds including organic metal complexes suffer physical and chemical changes when subjected to heat under defined experimental conditions. These changes are characteristic of substances and can be used for qualitative and quantitative analysis. The elimination of hydrated water molecules of the present mixed ligands metal complexes recorded on heating up to \sim 150 $^{\rm O}{\rm C}$ in the TG thermograms (Figure 2) the second

decomposition stage for all complexes involving the loss of BAC moiety, two coordinated water and lost species $3C_2H_2 + 5CO + 2H_2 + HBr$ (Table 4). The third step indicated by DTG within the temperature range 464-647°C of all complexes, resulting from the decomposition of NOR, a stable metal oxide are formed in case of complexes (2), (3), (4), and (6), $MnSO_4$ for complex (1) and Cu metal for complex (5) as a final residue. Kinetic and thermodynamic variables such as E*, H*, S*, and G* of the thermal process were computed using coats-Redfern^[47] and Horowitz-Metzger^[48] equations, as shown in Table 5. The E* values were found to be in the range $8.295-3.11 \times 10^5$ KJ mol⁻¹; the high values reflect the thermal stability of the complexes (Figure S3). The fact that the final residue free energy was larger than that of the starting compounds, suggesting that all breakdown processes were non-spontaneous, was proven by the positive sign of G* for complexes. The activation, G*, values

FIGURE 2 TGA and DTG diagram for NOR, BAC, and their metal complexes



for successive breakdown steps of a particular compound rose considerably. This seems to be attributable to the fact that significantly increasing S* quantities from one phase to the next exceeds the amounts of H*. On the other hand, the negative S* readings, indicated that the activated compound was better organized than the reactants or that the reaction was delayed.^[49–51]

3.4 | Antimicrobial efficiency

The data depicted in Figure 3 revealed that remarkable antimicrobial activities when all tested therapies shown antibacterial activity against all tested bacteria, particularly at higher tested doses and no antifungal observed (Table S2). The best bactericidal activity was observed in terms of *S. aureus* with the newly synthesized complex

(2) followed by (4), (5) and then (1), (3) compared with NOR and BAC. In respect to L. monocytogens, the complexes (1), (3) gave the highly significant followed by complex (6) with no significant variations for complexes (2), (5) in contrast to the NOR and BAC. In the case of B. cereus, the newly synthesized complexes (1), (3), (5), and (6) possess highly biological activity followed by complexes (2) and (4). In terms of A. baumanii shows no significant variations for complexes (1), (2), (4), and (5), and the complex (6) shows significant activity compared with NOR and BAC. The high sensitivity of the complexes have been attributed to hyper-conjugation of the coordinated aromatic Lewis bases, which increases the net electron density on the coordinated metal ion and consequently higher antimicrobial activity. In general, metal complexes are more active than the ligand because metal complexes may serve as a vehicle for

TABLE 4 The maximum temperature T_{max} (°C) and weight loss values of the decomposition stages for NOR, BAC, and their metal complexes

			Weight lo	oss (%)	
Compounds	Decomposition	T _{max} (°C)	Calc.	Found	Lost species
NOR	First step Second step Total loss Residue	116 330, 423, 654	8.77 83.69 92.46 7.54	8.75 83.73 92.48 7.52	$\begin{array}{l} C_2H_4\\ 6C_2H_2+3NO+HF+0.5H_2 \end{array}$
BAC	First step Total loss Residue	268	91.01 91.01 8.99	91.03 91.03 8.97	$3C_2H_2 + 3CO + HBr$ 2C
(1)	First step Second step Third step Total loss Residue	94 189, 440 641	4.45 37.46 29.05 70.96 28.93	4.34 37.22 29.10 70.66 29.32	$\begin{array}{l} 2H_2O\\ 3C_2H_2+5CO+2H_2+HBr\\ 3C_2H_2+3CO+3NH_3+HF+H_2\\ MnSO_4+7C \end{array}$
(2)	First step Second step Total loss Residue	213 464	39.15 45.35 84.5 15.5	39.11 45.37 84.48 15.49	$\begin{array}{l} 3C_2H_2+5CO+2H_2+HBr\\ 6C_2H_2+2NO_2+NH_3+HF+SO_2+H_2\\ FeO+4C \end{array}$
(3)	First step Second step Third step Total loss Residue	77 230, 403 560	6.7 37.59 31.51 75.8 24.2	6.68 37.61 31.48 75.77 24.21	$\begin{array}{l} 3H_{2}O\\ 3C_{2}H_{2}+5CO+2H_{2}+HBr\\ 2C_{2}H_{4}+2CO+3NH_{3}+HF+Cl_{2}\\ CoO+10C \end{array}$
(4)	First step Second step Third step Total loss Residue	94 241, 382 603	6.7 37.6 40.46 84.76 15.24	6.67 37.56 40.44 84.67 15.29	$\begin{array}{l} 3H_2O\\ 3C_2H_2+5CO+2H_2+HBr\\ 5C_2H_2+HF+NH_3+2HCl+2CO+H_2+N_2\\ NiO+4C \end{array}$
(5)	First step Second step Third step Total loss Residue	83 234, 378 647	4.54 38.22 49.2 91.96 8.04	4.52 38.19 49.29 92.01 7.96	$\begin{array}{l} 2H_{2}O\\ 3C_{2}H_{2}+5CO+2H_{2}+HBr\\ 7C_{2}H_{2}+HF+NH_{3}+Cl_{2}+2CO+N_{2}O\\ Cu \end{array}$
(6)	First step Second step Third step Total loss Residue	79.62 228, 342 557	4.39 36.97 41.37 82.73 17.27	4.36 36.98 41.35 82.69 17.28	$\begin{array}{l} 2H_{2}O\\ 3C_{2}H_{2}+5CO+2H_{2}+HBr\\ 4C_{2}H_{2}+3CO+SO_{2}+HF+2NH_{3}+NO+0.5H_{2}\\ ZnO+5C \end{array}$

activation of ligands as the principle cytotoxic species.^[52–55] Ciprofloxacin and moxifloxacin were utilized as standard material. The order of efficiency of the drug NOR and BAC mixed ligand metal complexes found as the following, in case of *S. aureus* decrease in order: complex (2) > complexes (4) and (5) > complexes (1) and (3) > ciprofloxacin standard > moxifloxacin standard > Nor > complex (6) > BAC, *L. monocytogens* decrease in order: complexes (1) and (3) > complex (6) > NOR > ciprofloxacin standard > BAC > moxifloxacin standard > complexes (2) and (5) > complex (4), *B. cereus* decrease in order: complex (5) > complex (1)

> complex (6) > complex (2) > complex (4)
> ciprofloxacin standard > moxifloxacin standard >
BAC > NOR, A. baumanii decrease in order: complex
(6) > BAC > NOR > moxifloxacin standard > ciprofloxacin standard > complex (4) > complex (2) > complexes
(1) and (5) > complex (3).

3.5 | Theoretical calculations

The optimized structures of the NOR, BAC, (1), (2), (3), (4), (5), and (6) compounds and related energies

TABLE 5 Thermal behavior and Kinetic parameters determined using Coats–Redfern (CR) and Horowitz–Metzger (HM) operated for NOR, BAC, and their metal complexes

				Parameter						
	Decomposition	Ts		E*		S*	H*	G*		
Compounds	range (K)	(K)	Method	(KJ/mol)	$A(s^{-1})$	(KJ/mol. K)	(KJ/mol)	(KJ/mol)	R ^a	SD ^b
NOR	537-734	696	CR	8.295	5.944×10^2	-1.958	7.716	2.135	0.921	0.310
			HM	11.585	6.838×10^4	-1.020	11.006	1.810	0.866	0.200
	844–996	927	CR	13.183	15.73×10^2	-1.357	12.412	2.499	0.934	0.190
			HM	14.512	14.68×10^3	-1.176	13.742	2.465	0.929	0.090
BAC	453-582	541	CR	127.59	2.59×10^{-6}	-0.357	-4.370	188.665	0.995	0.097
			HM	351.82	8.04×10^{6}	-0.118	-4.146	59.515	0.998	0.061
(1)	763–992	816	CR	2.73×10^{5}	3.25×10^{16}	0.066	268.355	232.410	0.965	0.222
			HM	3.11×10^5	4.65×10^{29}	0.318	306.045	133.344	0.963	0.225
(2)	322-557	487	CR	$6.16 imes 10^4$	3.11×10^5	-0.137	59.828	89.145	0.996	0.079
			HM	2.59×10^4	6.91×10^{5}	-0.130	24.106	52.003	0.992	0.117
(3)	750–933	833	CR	2.72×10^{5}	2.45×10^{14}	0.025	267.614	253.430	0.960	0.250
			HM	2.36×10^5	4.79×10^{21}	0.164	231.563	139.224	0.955	0.265
(4)	563-743	654	CR	$1.70 imes 10^5$	9.04×10^9	-0.056	167.106	188.575	0.962	0.259
			HM	9.18×10^4	1.42×10^{12}	-0.014	88.609	94.057	0.954	0.283
(5)	430–537	507	CR	9.39×10^4	8.90×10^8	-0.072	91.978	108.725	0.998	0.088
			HM	$5.05 imes 10^4$	1.00×10^{11}	-0.032	48.526	56.085	0.998	0.097
(6)	537-738	615	CR	1.62×10^5	2.75×10^9	-0.065	159.102	181.445	0.955	0.280
			HM	$7.02 imes 10^4$	1.85×10^{10}	-0.049	67.343	84.270	0.947	0.302

^aCorrelation coefficients of the Arrhenius plots.

^bStandard deviation.

were calculated utilizing DFT^[56] in addition to the B3LYP functional^[57,58] and Lee, Yang, Parr,^[59] as well as the Hartree-Fock local exchange function.^[60]

3.5.1 | Structural parameters and models of NOR

According to the calculated dihedral angles (Table S3), the NOR molecule is highly sterically hindered, and the piperazine group found out of the plane of molecule where the values are not zero or 180° and O5 found in *cis* configuration with O1 while O22 and O5 are in trans configuration and C21-O5 not in the same plane of C2-O22 (Figure 4). The value of bond angle reflects on sp² hybridization of C3; the same result is obtained with C2 and C4. The values of bond lengths are compared nicely with that obtained from X-ray data.^[61] The data of charge distribution on the optimized geometry of NOR (Table 6) indicate that a significant built up of charge density on the oxygen atoms which distributed over all molecule so NOR molecule behaves as bi-dentate ligand (O_{pyr} and O_{COOH}), and the molecule is a highly dipole $\mu = 42.86D$.

3.5.2 | Structural parameters and models of BAC

The calculated dihedral angle for the optimized geometrical of BAC (Table S4) confirms that the coumarin and carbonyl units are nearly planar. The end C1 = O6 and C4 = O10 of coumarin moiety bonds do not assume different orientations as predicted for binding of BAC as a bidentate ligand via the two carbonyl groups oxygen (O6 and O10), which lie in the same trend as the cis conformer (Figure 4). The average difference between B3LYP/CEP-31G and practical bond lengths and bond angles is 0.04 Å and 0.5°, respectively; these data are drawing to give the optimized geometry of molecule. The bond lengths and bond angles reflect that the type of hybridization sp^2 is common on all central atoms. The values of bond lengths, bond angles, and dihedral angles are compared nicely with that obtained from the experimental data.^[60-63] Because of the significant buildup of charge density on the donating oxygen atoms, the BAC compound reacts as a bi-dentate ligand (O6 and O10) with a highly dipole = 12.17D, which is credited to the



Control (DASO)

ciprofloxacit nothotacin



FIGURE 3 Statistical representation for biological activity of NOR, BAC, and their metal complexes

MISOA.6H2O



CuO2.2H2O

WC2.6H2O fe⁵⁰⁴

FIGURE 4 DFT-optimized geometry of NOR and BAC

30

25

20

15

10

5

0

Inhibitation diamater zone (mm)

molecule's planarity excluding the Br atom, which lies outside the plane dominated with all atoms of the molecule.

Geometrical structure of complexes 3.5.3

The main objective of this study is to determine the optimized structure of NOR, BAC, as well as their metal

complexes. Table S5 summarizes the bond lengths, bond angles, total energy, heat of formation, and dipole moment of each complexes. In all complexes metal ion is coordinated with six oxygen atoms (O1 and O5) of NOR, (O6 and O10) of BAC, and (O11 and O12) form water to complete the regular octahedral structure as shown in Figures S4–S9. The computational data (bond lengths and bond angles) show that the equatorial plane is dominated by four donors oxygen atoms, two from NOR

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TABLE 6 Calculated charges on donating sites and energy values (HOMO, LUMO), energy gap $\Delta E/eV$, hardness (η), global softness (S), electro negativity (χ), absolute softness (σ), chemical potential (Pi), global electrophilicity (ω), and additional electronic charge (ΔN_{max}) of NOR, BAC, and studied complexes by using DFT calculations

Parameters	NOR	BAC	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
М	-	-	0.587	0.163	0.302	0.140	0.075	0.226
01	-0.250	-0.283	-0.387	-0.366	-0.347	-0.363	-0.350	-0.366
O5	-0.340	-0.380	-0.447	-0.447	-0.372	-0.423	-0.365	-0.397
O6	-	-	-0.354	-0.297	-0.321	-0.257	-0.256	-0.356
O10	-	-	-0.326	-0.253	-0.296	-0.284	-0.286	-0.362
НОМО, Н	-0.376	-0.383	-0.379	-0.341	-0.352	-0.367	-0.359	-0.388
LUMO, L	-0.129	-0.161	-0.231	-0.235	-0.216	-0.219	-0.187	-0.185
I = -H	0.376	0.383	0.379	0.341	0.352	0.367	0.359	0.388
A = -L	0.129	0.161	0.231	0.235	0.216	0.219	0.187	0.185
$\Delta E = L - H$	0.247	0.222	0.148	0.106	0.136	0.148	0.172	0.203
$\eta = (I - A)/2$	0.124	0.111	0.074	0.053	0.068	0.074	0.086	0.102
$\chi = -(\mathrm{H}-\mathrm{L}/2)$	0.253	0.272	0.305	0.288	0.284	0.293	0.273	0.287
$\sigma = 1/\eta$	8.065	9.009	13.514	18.868	14.706	13.514	11.628	9.804
$S=1/2\;\eta$	4.032	4.505	6.757	9.434	7.353	6.757	5.814	4.902
$\mathrm{Pi}=-\chi$	-0.253	-0.272	-0.305	-0.288	-0.284	-0.293	-0.273	-0.287
$\omega = (Pi)^2/2~\eta$	0.258	0.333	0.629	0.782	0.593	0.580	0.433	0.404
$\Delta N_{max} = \chi/\eta$	2.041	2.450	4.122	5.434	4.176	3.959	3.174	2.814

Note: (I) is ionization energy and (A) is an electron affinity.

(O1 and O5), one of BAC (O6), and the latest from water molecule (O11), whereas the axial plane is inhabited by BAC and the second water molecule oxygen atoms (O10 and O12). The bond angle O11MO12 is in range (89.79° –90.05°), and this value refers to the two water molecules are lying in *cis*-form and then they are perpendicular to each other. Also, the angles around M(II) with surrounding oxygen atoms varied from 86.02° to 179.77°; these values not deviated from a regular octahedron. The bond lengths between metal ion and bonded oxygen atoms of NOR (O1 and O5) in all metal complexes varied from (1.925–2.086 Å) and (1.916–2.074 Å), respectively,^[64–68] also, the bond lengths between central metal ion and oxygen atoms of BAC (O6 and O10) are (1.922–2.079 Å) and (1.925–2.075 Å), respectively.^[69–76]

3.5.4 | Charge distribution analysis

The charge distribution of NOR indicates the presence of a greater net negative and positive pole on the molecule, as a result the molecule is a strong dipole, $\mu = 42.86D$. The charge density for NOR, BAC, and their complexes given in Table 6 show a relatively high charge density on the metal ion in the complexes (1) and (3) only; the charge accumulated on Mn(II) ion is 0.587 and 0.302 on

the Co(II) ion, while in case of other complexes, the metal ion carry lower charge density and the smallest charge is located on metal ion of complex (5). The negative charge was dispersed on the two ligands oxygen atoms, while all complexes hydrogen atoms afford positive sign. The NOR oxygen atoms (O1 and O5) have a higher negative charge than that of BAC in chelates. The charge density in studied complexes varies from 0.075 on the Cu-ion to 0.587 on Mn-ion (Table 6). These results mean that there is an electron back-donation from the metal sites in a MLCT mode to the π^* orbitals of the NOR in some of these complexes. This conclusion is further confirmed by comparing the values of the calculated charge density on the donating atoms, oxygen atom of NOR, BAC, and in complexes. The distribution of atomic charges is also important in the determination of the direction of the dipole moment vector in the complexes which depends on the centers of negative and positive charges.

3.5.5 | Molecular orbitals and frontier

Molecular orbitals play an important role in the electric properties.^[77] A system with a lower energy gap ΔE (the difference between HOMO and LUMO) was more



reactive than one with a larger ΔE .^[78] All studied complexes have lower ΔE than free ligands, so these complexes are more reactive; the values of ΔE (Table 6) varied from 0.106 eV for complex (2) (more reactive) and 0.203 eV for complex (6) (less reactive). The electron movement between orbitals easily occurs so we observe a peak around 250 nm in the UV-Vis spectra for all studied complexes, while the ΔE of the NOR and BAC is 0.247 eV and 0.222 eV, respectively. The ΔE is closely associated with the reactivity and stability of the executed molecule, and shows the nature of the molecule with low kinetic stability and slightly high chemical reactivity. On the other hand, the adjacent orbitals are often closely spaced on the frontier region. The nodal properties of molecular orbitals of studied complexes (Figure 5) are illustrative and suggest orbital delocalization, strong orbital overlap, and low number of nodal planes. These features lead to UV-Vis spectrum characterized by low energy and high intensity bands presence of charge transfer transitions. The different MO_s show a different extent

of localization on the different fragments of the complexes, and the above rationalization is valid for MO analysis of all the studied complexes. The ΔE for the all studied complexes varied according to the type of metal ion as shown in Table 6 and shows the isodensity surface plots of HOMO and LUMO for free ligands and their complexes. For NOR, the electron density of HOMO is delocalized and spreading over the all fragments of NOR ligand except terminal part of quinoline ring and terminal acetyl group, while the electron density of LUMO is delocalized and spread over all atoms in NOR molecule except piperazine ring only as shown in Table 6. The hardness (n) is defined as (n = (I - A)/2) where I is the ionization energy and A is the electron affinity. On the other hand, the (I - A) equals the gap between the HOMO and LUMO. As a result, the hardness of the compounds was determined by E, which may be computed as $n = \Delta E/2$. The results demonstrate that the all chelates were softer with n ranging from 0.053 to 0.102 but for NOR and BAC 0.124, 0.111, respectively.^[79,80]



FIGURE 5 Molecular orbital surfaces and energy levels of NOR, BAC and their metal complexes using DFT calculations

The electronic transition of complexes is easy as indicated from the ΔE of complexes which are in agreement with the values for stable transition metal complexes. For NOR, BAC, and their complexes, quantum chemical factors such as global softness (S), electro negativity (χ), absolute softness (σ), chemical potential (Pi), global electrophilicity (ω), and extra electronic charge (ΔN_{max}) were computed based on the energy values of HOMO and LUMO. According to these estimates, the complex (2) is ultimate soft ($\sigma = 18.868$ eV), whereas the complex (6) is hard complex ($\sigma = 9.804$ eV). NOR and BAC have (σ) of 8.065 eV and 9.009 eV, respectively.

3.5.6 | Excited state

The UV-Vis spectra were accurately described using time-dependent density functional response theory (TD-DFT) at the B3LYP level using the G03W software.^[80,81] The TD-DFT has subsequently been rewritten to calculate precise transition energies and oscillation strengths, and it has been used on a variety of atoms and molecules. In of excitation the computation the energies, Bauernschmitt and Ahlrichs^[82,83] used hybrid functionals. These hybrid techniques are usually a significant improvement over traditional Hartree-Fock (HF) based methods. The optimal architecture was determined in this study and was employed in all ensuing computations; the wave functions of SCF MOs were studied explicitly. The computed wave functions of the various MOs depict and imply the proportion of distinct complex pieces contributing to the overall wave functions of various phases. The findings show that there is a significant amount of electron delocalization in the various chemical orbitals. The electronic transition is a combination of $n \rightarrow \pi^*$ and $\pi \to \pi^*$ transitions. Table 6 lists the energies of the HOMO and LUMO states for NOR, BAC, and all investigated chelates. In a reaction profile, the HOMO can serve as an electron donor and the LUMO as an electron acceptor. In the complexes (3), (5), and (6), the electron density of HOMO is localized mainly on the peprazin ring only of NOR only, the electron density of HOMO in case of complex (4) localized on BAC and around central metal ion, while the electron density of HOMO in case of complex (2) localized mainly on peprazin ring and all donating oxygen atoms around the central metal ion, but in case of complex (1) the electron density of HOMO localized on the quinoline ring and the central metal ion with its surrounding donating oxygen atoms only. The electron density of LUMO in the complexes localized mainly on BAC molecules and small portion on central metal ion on the surrounding oxygen atoms but in case of complex (1) the electron density localized on peprazin ring only. As a

result, the electronic transition might be characterized as a mixture of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions with a tiny part on the peprazin ring, allowing for MLCT from metal ion to either BAC (π^*).

4 | CONCLUSION

Reactions of NOR and BAC with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions yielded new mononuclear complexes. The metal complexes were characterized and their structures clarified using various analytical and spectral techniques. The data showed that NOR and BAC functioned as bidentate ligands. All complexes have a coordination number of six. The results of the study back up the proposed octahedral architecture of metal complexes and produce a beneficial molecular arrangement. The Coats-Redfern and Horowitz-Metzeger techniques were used to determine kinetic parameters from the complexes' thermal degradation stages. Density functional theory calculations were carried out to investigate the optimized structure of the two ligands and their metal complexes and the obtained result indicate that there are agreement between the computed and experimental geometrical parameters is very good. The metal complexes had a stronger bactericidal impact than the ligands against several bacteria strains, including S. aureus, L. monocytogens, B. cereus, and A. bauamanii, but no antifungal action.

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AUTHOR CONTRIBUTIONS

Walaa El-Shwiniy: Formal analysis; software; supervision; validation; visualization; writing-original draft; writing-review and editing. Manar A. Gamil: Formal analysis; funding acquisition; investigation; methodology; project administration. Sadeek Sadeek: Supervision; validation; visualization; writing-review and editing. Wael A. Zordok: Conceptualization; data curation; software; validation; visualization.

CONFLICT OF INTEREST

This research holds no conflict of interest and is not funded through any source.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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