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Synthesis, spectroscopic and thermogravimetric interpretations of UO_2(II), ZrO(II), Zr(IV), VO(II) and V(V) ciprofloxacin antibiotic drug complexes

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New five ciprofloxacin (CIP) complexes of dioxouranium(II), oxozirconium(II), zirconium(IV), oxovanadium(II) and vanadium(IV) in the proportion 1:2 have been prepared using CIP as a drug chelate with $UO_2(NO_3)_2 \cdot 6H_2O$, $ZrOCl_2 \cdot 8H_2O$, $ZrCl_4$, $VOSO_4 \cdot xH_2O$ and V_2O_5 respectively. The CIP complexes have been characterized based on the elemental analysis, molar conductance, magnetic, (FTIR & ^{1}HNMR) spectral and thermal studies. The molar conductance studies of the synthesized complexes in DMSO solvent with concentration of 10^{-3} M indicate their non-electrolytic properties. At room temperature, the magnetic moment measurements revealed a diamagnetic behavior for all CIP prepared complexes. The different formulas of the new complexes can be represented as $[UO_2(CIP)_2(NO_3)_2]$ (**I**), $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**), $[V_2(O)(O_2)_2(CIP)_2]$ (**III**), $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**), and $[Zr(CIP)_2(Cl)_4]$ (**V**). The thermal analysis data of the complexes indicates the absence of coordinated water molecules except for vanadyl(II) complex (**II**). The CIP chelate is a uni-dentate ligand coordinated to the mentioned metal ion through terminal piperazinyl nitrogen. The transmission electron microscopy (TEM) investigation confirms the nano-structured form of the complexes.

Keywords: ciprofloxacin; complexation; FTIR; diamagnetic; TEM; nanoscale.

INTRODUCTION

Many drugs and active pharmaceutical agents included metal sites or metallo-pharmaceuticals binding, that can be coordinated or reacted with various metal ions and potentially influence their bioactivities and might also cause damages to their target biomolecules. Ciprofloxacin (CIP) antibiotic drug belongs to the fluoroquinolones family, which are bacteriostatic at low concentration and bactericidal at high concentrations[1–4]. The CIP drug has highly active against most Gram-negative pathogens including *Pseudomonas aeruginosa* and the *Enterobacteriaceae*. Fluoroquinolones are used to treat upper and lower respiratory infections, gonorrhea, bacterial gastroenteritis, skin and soft tissue infections and both uncomplicated and complicated urinary tract infections, especially those caused by Gram-negative than Gram-positive infections[2, 4]. Quinolones form metal chelates due to their ability to coordinated with different metal ions. In its metal complexes, the quinolones were reacted as a bi-dentate, unidentate and bridging bidentate ligand. Often, the quinolones are chelated in a bi-dentate manner via one of the oxygen atoms of deprotonated carboxylic group and the oxygen atom of carbonyl group. In rare cases, the quinolones can be chelated as bi-dentate ligand through oxygen atoms of carboxylic group or via two nitrogen atoms of piperazinyl ring. On the other hand, the quinolone drug can acts as a uni-dentate ligand towards the metal ion via the nitrogen atom of the terminal piperazinyl ring[5–25]. In literature survey, some of selected chelates of ciprofloxacin towards different metal ions can be metioned as: $[Mg(CIF)_2] \cdot 2.5H_2O$ [5], $[Mg(CIF)_2(H_2O)_2] \cdot 2H_2O$ [6], $[Mg(H_2O)_2(CIF)_2](NO_3)_2 \cdot 2H_2O$, $[Mg(CIF)_3](SO_4) \cdot 5H_2O$ [7], $[M(CIF)_2](ClO_4)_2 \cdot H_2O$ (M = Mg, Ca, Ba) [8], $[Mg(CIF)_2(H_2O)_2] \cdot 2H_2O$, $[Zn(CIF)_2] \cdot 3H_2O$, $[Co(CIF)_2] \cdot 3H_2O$ [9], $[(CIF)_3Al]$ [10], $[Bi(CIF)_3(H_2O)_2]$ [11], $[VO(CIF)_2(H_2O)]$ [12], $[Mn(CIF)(OAc)(H_2O)_2] \cdot 3H_2O$, $[Co(CIF)(OAc)(H_2O)_2] \cdot 3H_2O$, $[Ni(CIF)(OAc)] \cdot 6H_2O$, $[Cu(CIF)(OAc)(H_2O)_2] \cdot 3H_2O$, $[Zn(CIF)(OAc)] \cdot 6H_2O$, $[Cd(CIF)(OAc)(H_2O)_2] \cdot 3H_2O$ [13], $[Mn(CIF)_2(H_2O)_2]$, $[Fe(CIF)_3]$, $[Co(CIF)_2(H_2O)_2]$, $[Ni(CIF)_2(H_2O)_2]$, $[MoO_2(CIF)_2]$ [14], $[Co(CIF)_2(H_2O)] \cdot 9H_2O$, $[Zn(CIF)_2(H_2O)_2] \cdot 8H_2O$, $[Cd(CIF)_2(Cl)_2] \cdot 4H_2O$, $[M(CIF)_2] \cdot xH_2O$ (M = Ni, Cu, Cd) [15], $[Co(CIF)_2] \cdot 3H_2O$ [16], $[Cu(CIF)_2](NO_3)_2] \cdot 6H_2O$ [17], $[Cu(CIF)_2]Cl_2 \cdot 11H_2O$ [18], $[Cu(CIF)_2]Cl_2 \cdot 6H_2O$ [19], $[Cu(CIF)_2(ClO_4)_2] \cdot 6H_2O$, $[Cu(CIF)_2(NO_3)_2] \cdot 6H_2O$, $[Cu(CIF)(C_2O_4)] \cdot 2H_2O$ [20], $[Cu^{II}(CIF)_2(Cu^{I}Cl_2)_2]$ [21], $[Ru(CIF)_2Cl_2]Cl \cdot 3H_2O$ [22], $[Ru(CIF)_3] \cdot 4H_2O$ [23], $[PdCl_2(CIF)]$ [24], $[Eu(HCIF)(Cf)(H_2O)_4]Cl_2 \cdot 4.5H_2O$ [25]. The preparation and characterization of new metal complexes with ciprofloxacin antibacterial agents are of great importance for understanding the drug-metal interaction and taking into account their potential pharmacological use. The aim of this article is the isolation and spectroscopic characterization of the UO_2(II), ZrO(II), Zr(IV), VO(II) and V(V) complexes, as well as their structural using spectroscopic and thermal analysis techniques.

EXPERIMENTAL

Chemicals and instruments

All chemicals used in this study were of analytical reagent grade. The ciprofloxacin drug, $UO_2(NO_3)_2 \cdot 6H_2O$, $ZrOCl_2 \cdot 8H_2O$, $ZrCl_4$, $VOSO_4 \cdot xH_2O$ and V_2O_5 were purchased from Sigma-Aldrich Chemical Company and used without further purification. The instrumental analyses and their models are listed as follows:

1. Analysis: elemental analyses; conductance; FTIR spectra; 1HNMR spectra; electronic spectra; magnetic moment; thermogravimetric; TEM.

2. Models: Perkin Elmer CHN 2400; Jenway 4010 conductivity meter; Bruker FTIR Spectrophotometer; Varian Mercury VX-300 NMR spectrometer, 300 MHz; UV2 Unicam UV/Vis Spectrophotometer; Magnetic Susceptibility Balance; TG/DTG–50H, Shimadzu thermo-gravimetric analyze; JEOL 100s microscopy.

Synthesis of CIP complexes

The dioxouranium(II), oxozirconium(II), zirconium(IV), oxovanadium(II) and vanadium(IV) ciprofloxacin complexes were synthesized by utilizing a 1:2 stoichiometry between metal ions and CIP ligand. A solution of 1.0 mmol of a metal ions $UO_2(NO_3)_2 \cdot 6H_2O$, $ZrOCl_2 \cdot 8H_2O$, $ZrCl_4$, $VOSO_4 \cdot xH_2O$ and V_2O_5 that previously soluble in 20 mL of distilled water was mixed to 2.0 mmol of ciprofloxacin drug suspended in 50 of acetone solvent. The mixtures were continuously stirring with heated at ~ 60°C under reflux on a hotplate for about 15 hrs and then cooling overnight. The associated solid complexes were isolated by filtration, washed several times with 20 mL boiling water and 10 mL acetone then dried under *vacuum* over anhydrous $CaCl_2$. After the dissolved of oxozirconium(II), zirconium(IV), oxovanadium(II) complexes in concentrated nitric acid, the presence of Cl^- and $SO_4^{-\ -}$ ions inside the coordination sphere of CIP complexes were investigated by using the $AgNO_3$ and $BaCl_2$ reagents. The yield of the products was about 71–78%. The solid complexes have a higher melting point above 250°C. The elemental analyses (Calc./Found) and physical meaning of the CIP complexes can be listed in Table 1.

RESULTS AND DISCUSSIONS

Elemental analysis and conductance measurements

The elemental analysis vales and some of the physical meaning (color and molar conductance), as well as the magnetic susceptibility of the dioxouranium(II), oxozirconium(II), zirconium(IV), oxovanadium(II) and vanadium(IV) ciprofloxacin complexes (I–V), are introduced in Table 1. All synthesized CIP complexes are colored, slightly hygroscopic and thermally stable with high melting points, indicating a strong metal-ligand interaction. The five solid CIP complexes are insoluble in most common organic solvents like ethyl alcohol, chloroform, diethyl ether, benzene, cyclohexan, carbon tetrachloride, but are partially soluble in DMSO and DMF solvents. The elemental analysis data (Table 1) of UO_2(II), ZrO(II), Zr(IV), VO(II) and V(V) complexes are consistent with their general formulation as 1:2 ratio of the type $[UO_2(CIP)_2(NO_3)_2]$ (**I**), $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**), $[V_2(O)(O_2)_2(CIP)_2]$ (**III**), $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**), and $[Zr(CIP)_2(Cl)_4]$ (**V**). The molar conductance data of the complexes in DMSO with gently heating at 10^{-3} M concentration are found to be (Λ_m = 7−24) $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$, that indicating their non-electrolytic behavior[26]. Because of failed to isolate a pure single crystal, the X-ray crystal structure was not performed. Therefore, the solid complexes were interpreted based on the elemental analysis, FTIR, ^{1}H-NMR, TG/DTG analysis.

Infrared spectra

FTIR spectra of the five CIP complexes are shown in Fig. 1a−c. The infrared frequencies of ciprofloxacin drug and UO_2(II), ZrO(II), Zr(IV), VO(II) and V(V) complexes (Table 2) were assigned.

i. *$[UO_2(CIP)_2(NO_3)_2]$ (**I**) complex*

The FTIR spectrum of the $[UO_2(CIP)_2(NO_3)_2]$ (**I**) complex (Fig. 1a) shows distinguish frequencies at 1731 cm^{-1} and 1628 cm^{-1} which are assigned to ν(C=O) of carboxylic and carbonyl groups. These vibration bands are occur at the same or shifted to higher frequencies in

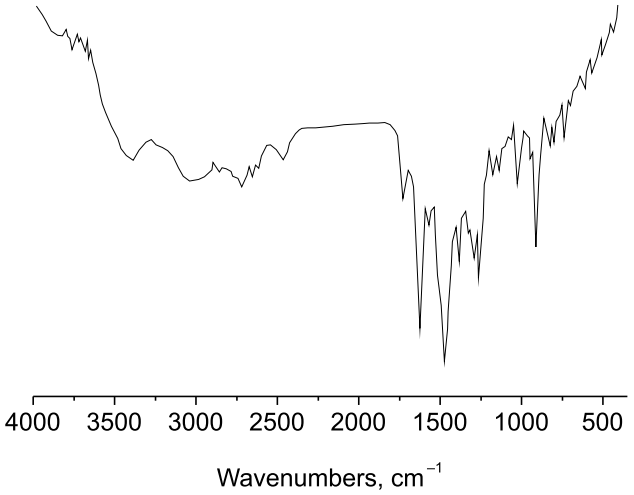


Figure 1a. FTIR spectrum of $[UO_2(CIP)_2(NO_3)_2]$ (**I**) complex

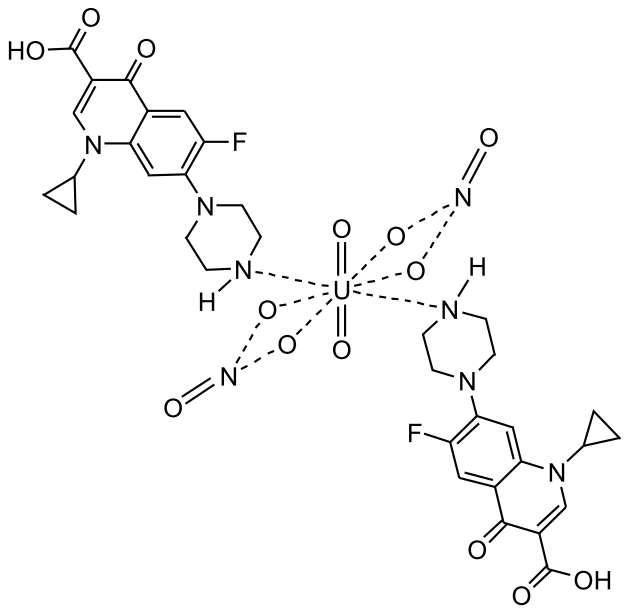
Table 1. Elemental analysis and physical properties of CIP complexes

Complex	Color	Magnetic moment (BM)	Conductance ($ohm^{-1} \cdot cm^2 \cdot mol^{-1}$)	Element (%)	Calc.	Found
I	Yellow	Diamagnetic	22	C	38.64	38.43
				H	3.43	3.32
				N	10.60	10.02
				M	22.53	22.43
II	Yellowish green		17	C	48.40	48.21
				H	4.54	4.50
				N	9.96	9.91
				M	6.04	5.98
III	Green		7	C	48.35	48.22
				H	4.30	4.21
				N	9.95	9.89
				M	12.06	12.03
IV	Light Yellow		11	C	48.57	48.55
				H	4.32	4.31
				N	10.00	9.95
				M	10.85	10.80
V	Yellow		24	C	45.59	45.52
				H	4.05	4.02
				N	9.38	9.33
				M	10.18	10.09

comparison with the free CIP drug (1707 cm^{-1} and 1627 cm^{-1})[19–25]. These results confirmed that the oxygen atoms of carboxylic and carbonyl groups didn't participate in the coordination towards UO_2(II) metal ions. Therefore, ciprofloxacin ligand acts as a neutral mono-dentate and coordinated to UO_2(II) metal ion through –N atom of piperazinyl ring. This coordination mode rarely took place and, to this knowledge, unprecedented in quinolone drug interactions toward metal ions. The presence of four new absorption bands at 1568, 1298, 1037, and 747 cm^{-1} corresponding to ν_4, ν_1, ν_2 and ν_3 vibrations agree with frequencies reported for bi-dentate nitrate group[27]. These frequencies values confirmed that the nitrate group is located inside the coordination sphere[27]. If the difference between ($\nu_4 - \nu_1$) is near to ~200 cm^{-1}, it's favored that the nitrate group has a covalency character[27] for the metal-nitrate chelating. The separation of highest frequency bands ν_1 and ν_4 (180–140 cm^{-1}) in the complexes favors bidentate character of the nitrate group[27]. Accordingly, the most probable geometrical structure of this complex is shown in Formula A, where the two nitrato groups act as bidentate chelates while the two CIP molecules exhibit as mono-dentate ligands. The FTIR spectrum of UO_2(II) complex show two absorption bands at 919 cm^{-1} and 838 cm^{-1} assigned to ν_{asym}(O-U-O) and ν_{sym}(O-U-O) vibrational modes of linear O=U=O moiety[28, 29]. The weak absorption bands presence at frequencies 570, 501, and 436 cm^{-1} are assigned to the coordination bonds ν(M-O) and ν(M-N) between UO_2(II) metal ion and oxygen atoms of nitrato groups and nitrogen atom of CIP moieties respectively[30].

ii. *$[VO(CIP)_2(SO_4)(H_2O)]$ (**II**) and $[V_2(O)(O_2)_2(CIP)_2]$ (**III**) complexes*

The infrared spectra of the $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**) and $[V_2(O)(O_2)_2(CIP)_2]$ (**III**) complexes are displayed in Fig. 1b and their band assignments are given in produced in Table 2. The FTIR spectra of these complexes have two distinct bands at 1707 cm^{-1} and ~1620 cm^{-1} attributed to



Formula A. Suggested structure of $[UO_2(CIP)_2(NO_3)_2]$ (**I**) complex

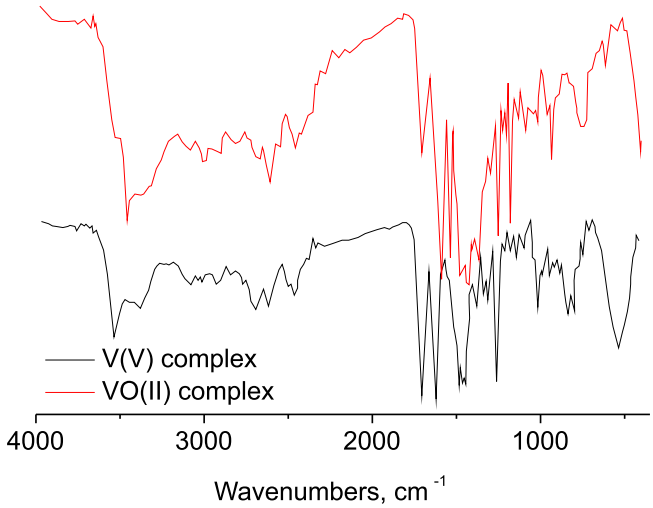


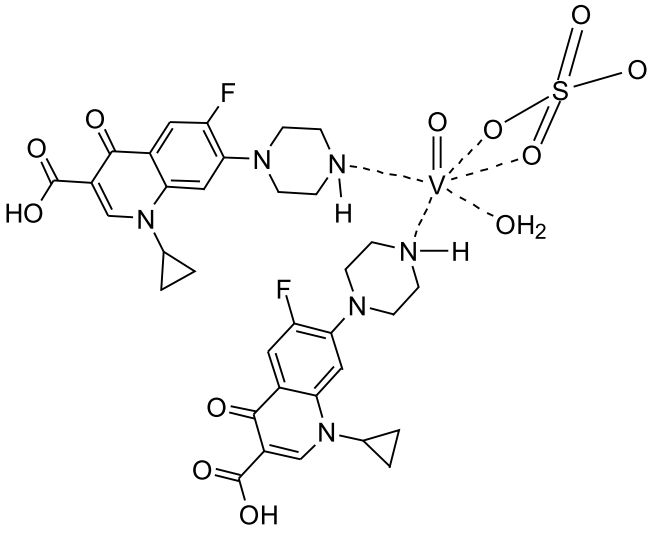
Figure 1b. FTIR spectrum of $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**) and $[V_2(O)(O_2)_2(CIP)_2]$ (**III**) complexes

Table 2. IR frequencies (cm^{-1}) and assignments of CIP and its five complexes

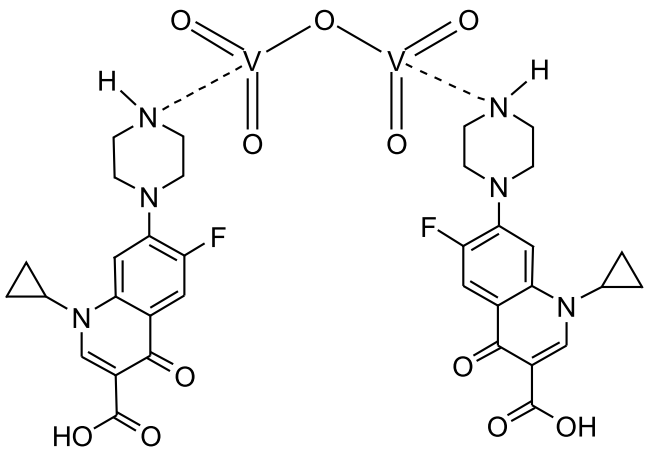
CIP	UO_2(II)	VO(II)	V(V)	ZrO(II)	Zr(IV)	Assignments
3084 2924	3028	3086	3085	3027	3024	ν_s(O-H); H_2O ν (C-H)
1707	1731	1707	1707	1733	1732	ν(C=O): (COOH)
1627	1628	1623	1624	1628	1628	ν(C=O) + $\delta_b(H_2O)$
1495 1449	1568 1478	1490 1451	1483 1450	1509 1474	1473	CH_2; deformation ν(N=O): NO_3 (ν_1)
1342	1388	1384	1384	1392 1331	1393	$\delta_b(CH_2)$
–	1298	–	–	–	–	ν(N-O): NO_3 (ν_4)
1273 1221	1267	1308 1271	1270	1264	1265	ν(C-C) + ν(C-O) + ν(C-N)
1144 944	1183 1148 1037	1190 1154 1106 1044	1144 1106 1023	1187 1037	1187 1036	ν(N-O): NO_3 (ν_2) $\delta_r(CH_2)$ ν(S-O) (ν_3)
–	919 838	978 833	944 831	955	–	ν(U=O) ν(V=O) ν(Zr=O)
805 750	747 624	805 753 627	750	746 705 628	746	CH- bend δ(NO_2): NO_3 (ν_3) δ(OSO) (ν_4)
–	570 501 436	540 476	537 415	570 502 433	569 499 475	ν(M-O) + ν(M-N)

ν, stretching; δ, bending.

ν(C=O) of –COOH and ν(C=O) of pyridone ring. These vibration bands were exhibited at the same frequencies of CIP free ligand, this supported that the coordination site far away from oxygen atoms of both carboxylic and pyridone ring of the CIP drug ligand. So, the expected chelation of CIP towards VO(II) and V(V) metal ions occurs through the nitrogen atom of piperazinyl ring as a neutral monodentate ligand (Formula B & C).



Formula B. Suggested structure of $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**) complex



Formula C. Suggested structure of $[V_2(O)(O_2)_2(CIP)_2]$ (**III**) complex

In the case of $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**) complex, the coordination of sulfato group towards vanadium metal ions in a bi-dentate chelation and the ν_3 and ν_4 modes may be split[27, 30]. Regarding, the vanadyl(II) sulfato complex ($[VO(CIP)_2(SO_4)(H_2O)]$ (**II**), the bidentate chelation of the sulfato group is assigned by the presence of bands at 1106 cm^{-1} and 627 cm^{-1} that attributed to ν(S-O); ν_3 and δ(OSO); ν_4 respectively, which characteristic for the tetrahedral T_d point group. The stretching vibration motions of υ(S-O); ν_1 and δ(OSO); ν_2 are IR-inactive. On the other hand, the infrared spectra of VO(II) and V(V) complexes show a medium absorption band at 987–944 cm^{-1} and 833–831 cm^{-1} attributed to ν(V=O)[31]. The new absorption bands at regions 540–538 cm^{-1} and 476–415 cm^{-1} are assigned to M-O and M-N stretching vibration motions[30].

iii. *$[Zr(O)(CIP)_2(Cl)_2]$ (**IV**) and $[Zr(CIP)_2(Cl)_4]$ (**V**) complexes*

Figure 1c show the infrared spectra of $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**) and $[Zr(CIP)_2(Cl)_4]$ (**V**) complexes. By comparison between the vibration frequencies of free CIP drug ligand and two zirconium(**IV**/**V**) complexes, it was found that there are two absorption bands in the case of free CIP ligand at 1707 cm^{-1} and 1627 cm^{-1}. The first band at 1707 cm^{-1} is assigned to the carboxylic group, this band was observed in the spectra of the zirconium(**IV**/**V**) complexes with shifted to the higher frequency at ~ 1730 cm^{-1}, indicating that the carboxylic group didn't share in the coordination towards metal ion. The other stretching vibration band presence at 1627 cm^{-1} is assigned to the ketone group, this band existed at 1628 cm^{-1} in the spectra of zirconium(**IV**/**V**) complexes in the same position of the CIP ligand, so it could be assigned to the uncoordinated of the ketone group towards metal ion. Similar to the UO_2(II), VO(II) and V(V) complexes, the nitrogen atom of the piperazinyl ring is involved in the coordination to zirconium metal ion as shown in Formula D&E. The ν(Z=O) vibration in the $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**) complex is observed as the expected frequency at 955 cm^{-1} is a good agreement with those known for many zirconyl(II) complexes[27, 30].

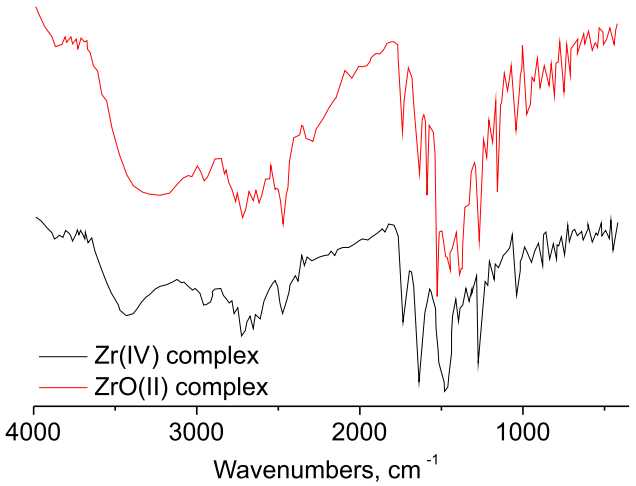
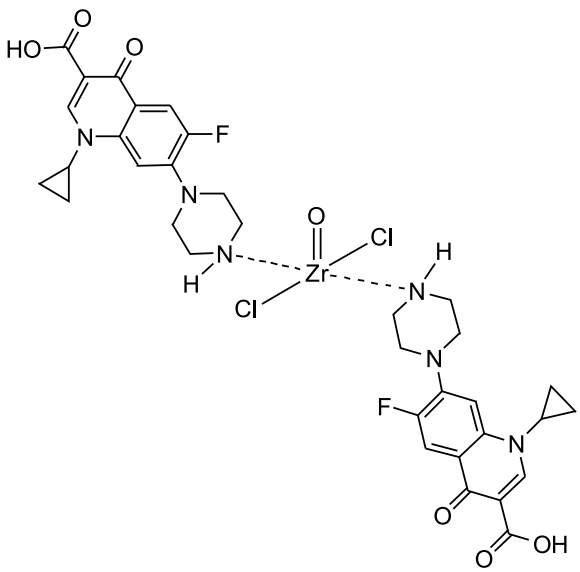
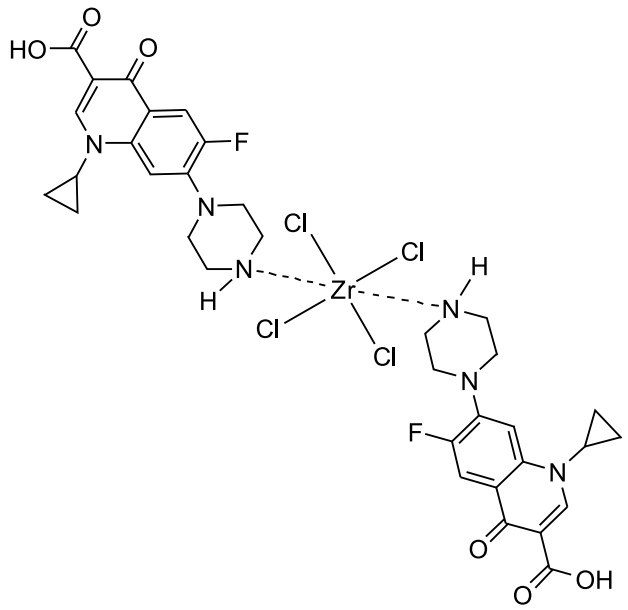


Figure 1c. FTIR spectrum of $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**) and $[Zr(CIP)_2(Cl)_4]$ (**V**) complexes



Formula D. Suggested structure of $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**) complex



Formula E. Suggested structure of $[Zr(CIP)_2(Cl)_4]$ (**V**) complex

Electronic spectra and magnetic susceptibility

The electronic absorption spectra of the UO_2(II), ZrO(II), Zr(IV), VO(II) and V(V) ciprofloxacin complexes dissolved in DMSO solvent were scanned within the UV-Vis (200–800 nm) region. In the case of the CIP free ligand, there are two distinguish bands that were present at 275 and 325 nm due to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electronic transitions of the hydrocarbons, carboxylic and ketonic moieties. The absorption spectra of all synthesized complexes are similar to the free CIP ligand with slightly shifted, these can be confirmed that the CIP ligand didn't change to the zwitterionic structure and both carboxylic and carbonyl groups not involved in the complexation towards metal ions. The magnetic susceptibility values of the dioxouranium(II), oxozirconium(II), zirconium(IV), oxovanadium(II) and vanadium(IV) ciprofloxacin complexes (**I-V**) were calculated and revealed a diamagnetic nature of the complexes[32, 33].

^{1}HNMR spectra

The ^{1}HNMR spectral assignments of CIP free ligand and UO_2(II), ZrO(II) and V(V) complexes are listed in Table 3 in order to recognize the coordination site. The ^{1}HNMR spectra of $[UO_2(CIP)_2(NO_3)_2]$ (**I**), $[V_2(O)(O_2)_2(CIP)_2]$ (**III**), and $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**) complexes in DMSO-d_6 showed frequencies at δ (15.00, 8.45–8.62, 7.84, 7.53, 3.30, 3.50, 2.08, 3.35, 9.05, 3.84, 1.38 & 1.27), (15.11, 8.65, 7.86, 7.50, 3.26, 3.52, 2.09, 3.49, 9.64, 3.82, 1.21 & 1.41) and (15.00, 8.41-8.66, 7.86, 7.55, 3.28, 3.63, 2.08, 3.46, 10.03, 3.89, 1.34 & 1.17) ppm respectively. These chemical shifts are located at the same ppm as mentioned in the case of free CIP drug (15.14, 8.69, 7.95, 7.61, 3.33, 3.59, 2.08, 3.37, 9.55, 3.88, 1.34 & 1.21) ppm except for δ H; NH signal of piperazine and aromatic rings in comparison with the free CIP drug, which was affected after chelation and shifted to up or downfield. The proton of the –COOH group didn't change and present at the same chemical shift, this meaning that the carboxylic group not participated in coordination process. The structures of the complexes of ciprofloxacin with UO_2(II), ZrO(II), Zr(IV), VO(II) and V(V) ions have been confirmed from the elemental analyses, FTIR, molar conductance, UV-Vis and thermal analysis data. Thus, from the FTIR spectra, it is concluded that ciprofloxacin behaves as a neutral unidentate ligand coordinated to the metal ions via the piperazine N atom. From the molar conductance data, it was found that the complexes are non-electrolytes. As a general formula, the investigated complexes structures can give as shown in Formulas A-E.

Thermo gravimetric analysis

In the present study, the heating rate was 10°C/min under N_2 atmosphere and the mass loss was scanned from

Table 3. ^{1}HNMR spectral data of CIP drug and UO_2(II), ZrO(II) and V(V) complexes

Protons	Chemical Shifts (δ, ppm)			
	CIP	UO_2(II)	ZrO(II)	V(V)
COOH	15.14	15.00	15.00	15.11
2	8.69	8.45–8.62	8.41–8.66	8.65
5	7.95	7.84	7.86	7.86
8	7.61	7.53	7.55	7.50
2'	3.33	3.30	3.28	3.26
3'	3.59	3.50	3.63	3.52
5'	2.08	2.08	2.08	2.09
6'	3.37	3.35	3.46	3.49
4'; NH	9.55	9.05	10.03	9.64
1"	3.88	3.84	3.89	3.82
2"	1.34	1.38	1.34	1.21
3"	1.21	1.27	1.17	1.41

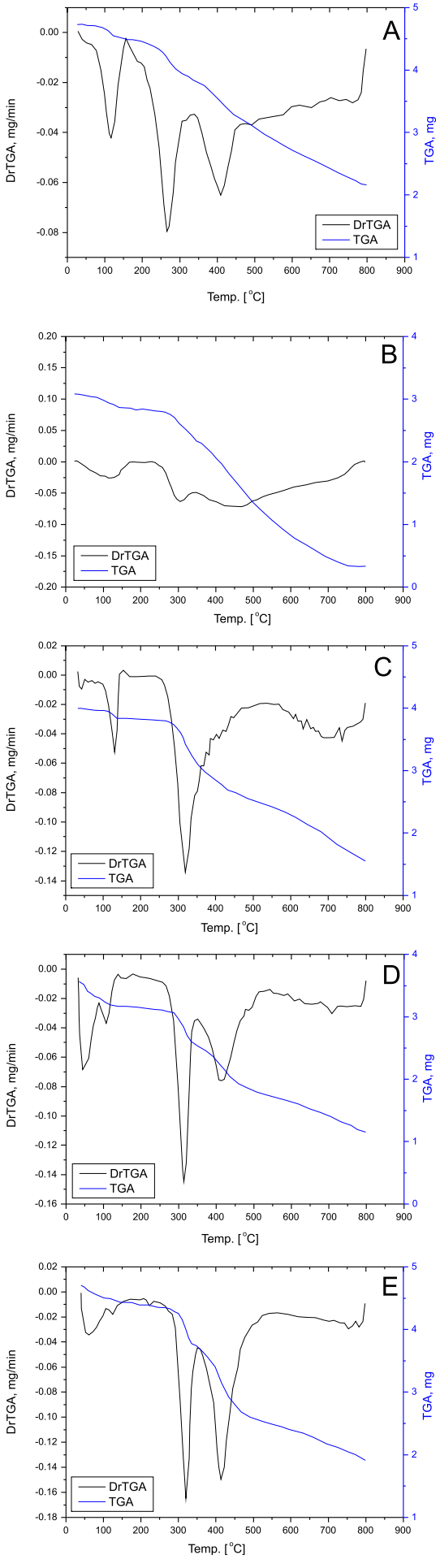


Figure 2. TGA and DrTGA curves of A: $[UO_2(CIP)_2(NO_3)_2]$, B: $[VO(CIP)_2(SO_4)(H_2O)]$, C: $[V_2(O)(O_2)_2(CIP)_2]$, D: $[Zr(O)(CIP)_2(Cl)_2]$, and E: $[Zr(CIP)_2(Cl)_4]$ complexes

room temperature to 800°C (Fig. 2A–E). The thermal cracking of $[UO_2(CIP)_2(NO_3)_2]$ (**I**) complex takes place through three DrTGA steps. The first occurs at 118°C and it corresponds to the mass loss of 17.71% with the elimination of nitrato coordinated groups and other terminal groups. The second step presence at 268°C due to the start decomposition of CIP molecules with a mass loss 20.90%. The third decomposition step at 410°C is assigned to the contentious decomposition of CIP molecule with a mass loss 15.21%. The UO_2 oxide which was polluted with few un-oxidized carbon atoms is the final residual solid product at 800°C. The $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**) complex was thermally decomposed within four thermal decomposition steps at DrTGA = 134, 302, 470 and 730°C, the first step is assigned to the loss of two-terminal propyl molecules with mass loss of 8.32%. The second, third and fourth steps are attributed to the loss of one of coordinated H_2O, SO_4 and 2CIP molecules with a mass loss of 81.60%. The final residual solid Blue-black powder at 800°C was vanadium oxide VO_2. The thermal destruction of $[V_2(O)(O_2)_2(CIP)_2]$ (**III**) occurs at three steps. The decomposition step occurs at temperatures 133, 318 and 737°C corresponds to the elimination of 2CIP molecules with mass loss of 60.69%. The V_2O_5 contaminated with few un-oxidized carbon atoms are the final residual product at 800°C. The thermal decompositions of $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**), and $[Zr(CIP)_2(Cl)_4]$ (**V**) complexes occurs within two-to--three steps at differential thermogravimetric peaks (109, 315 & 415°C) and (320 & 414°C) respectively. These degradation peaks correspond to the decomposition of ciprofloxacin and chlorine molecules with mass loss of 67.14 and 58.88% for complexes **IV** and **V** respectively. In both zirconium complexes, the ZrO_2 oxide polluted with few carbon atoms is the final remaining product at 800°C.

TEM investigation

The transmission electron microscopy images of the $[UO_2(CIP)_2(NO_3)_2]$, $[VO(CIP)_2(SO_4)(H_2O)]$, $[V_2(O)(O_2)_2(CIP)_2]$, $[Zr(O)(CIP)_2(Cl)_2]$, and $[Zr(CIP)_2(Cl)_4]$ complexes are shown in Fig. 3, all complexes have a nanostructured form with a nanoscale range of nm, respectively.

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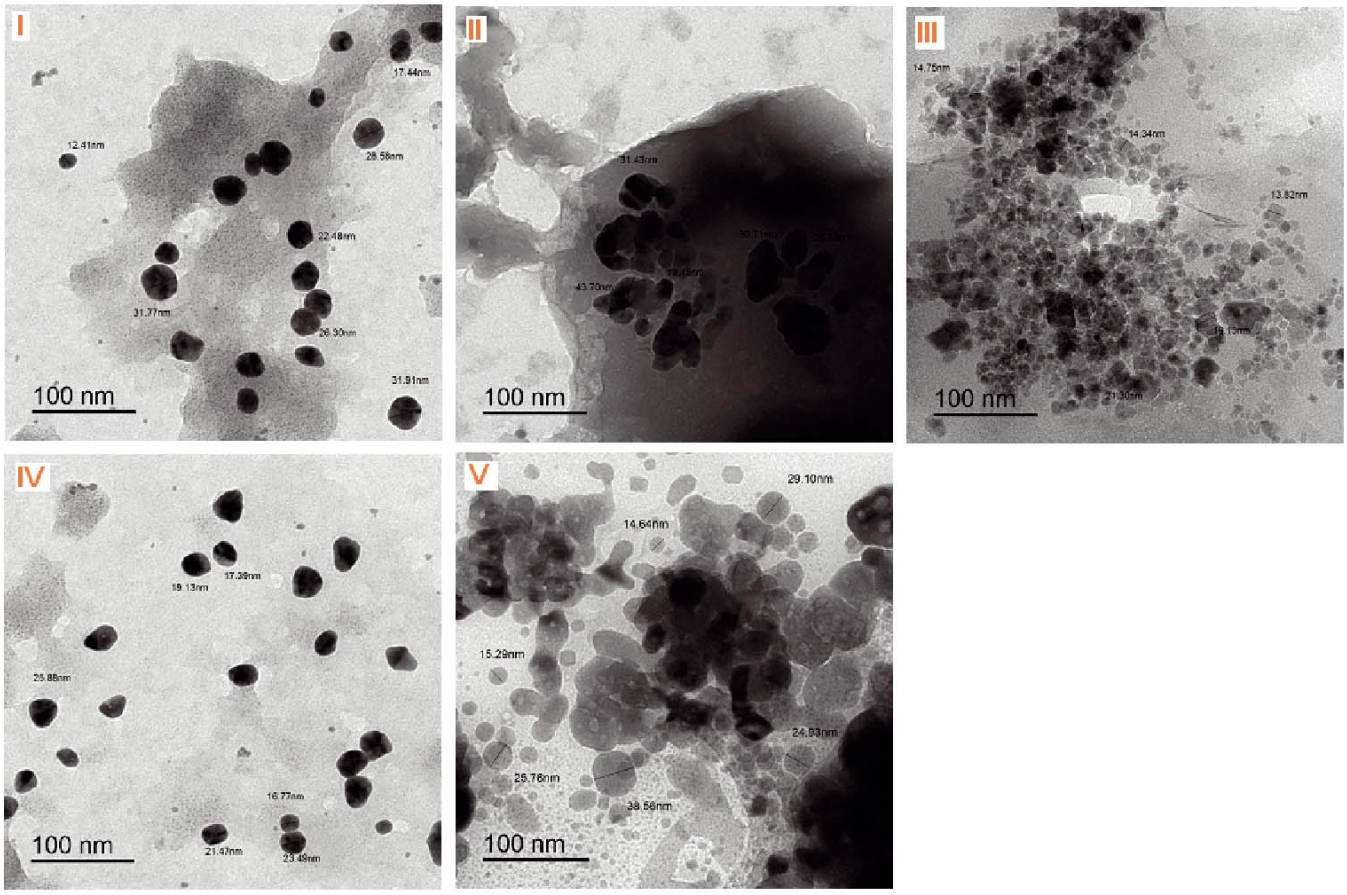

Figure 3. TEM images of $[UO_2(CIP)_2(NO_3)_2]$ (**I**), $[VO(CIP)_2(SO_4)(H_2O)]$ (**II**), $[V_2(O)(O_2)_2(CIP)_2]$ (**III**), $[Zr(O)(CIP)_2(Cl)_2]$ (**IV**), and $[Zr(CIP)_2(Cl)_4]$ (**V**) complexes

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