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RESEARCH ARTICLE

Synthesis, characterization and antimicrobial studies on $[VO(Lom)_2L]Cl_3$ (L=DMF, An, Py, o-Tol and Et_3N)

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Abstract

Five coordinated oxovanadium(V) complexes with lomefloxacin and various monodentate have been prepared. The structure of complexes has been investigated using physicochemical, spectral, elemental analysis as well as thermogravimetric analysis. The data indicate that the lomefloxacin reacted as a bidentate ligand through the pyridone group and one oxygen of carboxylic group. The antimicrobial activities of the complexes, ligands, metal salt and some standard drugs have been evaluated against *Staphylococcus aureus* (*S. aureus*), *Bacillis subtilis* (*B. subtilis*) and *Streptococcus pyogenes* (*S. pyogenes*) as gram positive bacteria and *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa* (*P. aeruginosa*) and *Klebsiella pneumonia* (*K. pneumoniae*) as gram negative bacteria. The result shows the significant increase in the antibacterial activity of the ligand on complexation.

INTRODUCTION

The term quinolone is commonly used for the quinolone carboxylic acids which are a group of synthetic antibacterial agents. Modifications of nalidixic acid were made based on structure activity relationships. It was discovered that a fluorine atom at position 6 and a piperazine ring at position 7 greatly enhance the spectrum of activity against aerobic gram negative microorganisms but less active against gram positive microorganisms [1, 2].
Quinolone antibiotics are complexing agents for a varity of metal ions including alkaline earth metal ions. In these complexes the quinolone acts as a bidentate ligand through the ring carbonyl group at position 4 and through one of the oxygen atoms of the carboxylato group at position 3. Quinolones can also act as bridging ligands and thus capable of forming polynuclear complexes [3, 4].

In this context, the interaction of V(V) with lomefloxacin in presence of dimethyl fomamide, aniline, orthotoludine, pyridine and triethyl amine has been studied in an attempt to examine the mode of binding and possible synergetic effects. The resultant mononuclear complexes have been characterized with elemental analysis, spectroscopic (IR, UV-vis., ^{1}H NMR) techniques and thermogravimetric analysis.

Materials and methods

All chemicals used for the preparation of the complexes were of analytical reagent grade, commercially available from different sources. lomefloxacin used in this study were obtained from EIPICO, VOCl (99.9%) was purchased from Aldrich Chemical Co. and solvents were purchased from Merck. These materials used without further purification. The infrared spectra of the five solid complexes and lomefloxacin were recorded from KBr discs using FTIR460 plus, ^{1}HNMR spectra were recorded on Varian Mercury VX-300 NMR Spectrometer using DMSO-d as solvent.C, H and N elemental analysis were carried out on a Perkin Elmer CHN 2400. The percentage of V(V) was determined gravimetrically by transforming the solid products into vanadium(V)oxide and also determined by using atomic absorption method. A spectrometer model PYEUNICAMSP 1900 fitted with the corresponding lamp was used for this purposed. Electronic solid reflection spectra of lomefloxacin and the isolated solid complexes were obtained in the region of 800–200 nm using UV-3101PC Shimadzu with a 1 cm quartz cell. Thermogravimetric (TG) and differential (DTG) thermogravimetric analysis were carried out under N-atmosphere using detectors model TGA 50H Shimadzu. The rate of heating of the sample was kept at 10°C/min. Molar conductivities in DMSO at $1.0x10^{-3}$M for all compounds were measured on CONSORT K410.

Synthesis of lomefloxacin metal complexes

An ethanolic suspended solution (20 mL) of lomefloxacin (1.0 mmol, 0.388 g) was added to an ethanolic solution of $VOCl_3$ (0.5 mmol, 0.095 mL) and the reaction mixture was stirred at room temperature for 1h and then adding 1 mL dimethylformamide (0.5 mmol, d=0.949) after that the mixture was stirred for 3 days at room temperature. The solution was left for slow evaporation, after that a dark green $[VO(Lom)_2DMF]Cl_3$ product was deposited. The solid obtained was filtered under vacuum, washed with ethanol and dried over anhydrous $CaCl_2$. In similar way described above, the black, brown, black and yellow $[VO(Lom)_2An]Cl_3$, $[VO(Lom)_2Py]Cl_3$, $[VO(Lom)_2o\text{-}Tol]Cl_3$ and $[VO(Lom)_2Et_3N]Cl_3$ complexes were prepared by using ethanol as a solvent and using Aniline, Pyridine, o-toluidine, triethylamine instead of DMF in 1:2:1 molar ratio.

Unfortunately we were not able to obtained appropriate monocrystals to perform X-ray diffraction analysis. The qualitative reactions revealed the presence of chloride as counter ions.

Antibacterial activity

Antibacterial activity of the ligand and its metal complexes was investigated by a previously reported modified method of Beecher and Wong [5] against different bacterial species, such as three Gram-negative *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa* (*P. aeruginosa*) and *Klebsiella pneumonia* (*K. pneumoniae*) and three Gram-positive, *Staphylococcus aureus* (*S. aureus*), *Bacillis subtilis* (*B. subtilis*) and *Streptococcus pyogenes* (*S. pyogenes*) microorganisms. The nutrient agar medium for antibacterial was (0.5% Peptone, 0.1% Beef extract, 0.2% Yeast extract, 0.5% NaCl and 1.5% Agar-Agar) was prepared and then cooled to 47 °C and seeded with tested microorganisms. After solidification 5 mm diameter holes were punched by a sterile cork-borer. The investigated compounds, i.e., ligand and their complexes, were introduced in Petri-dishes (only 0.1 ml) after dissolving in DMSO at 1.0×10^{-3} M. These culture plates were then incubated at 37 °C for 20 h for bacteria. Theactivity was determined by measuring thediameter of the inhibition zone (in mm). Growth inhibition was calculated with reference to the positive control, i.e., lomfloxacin.

Results and discussion

Lomefloxacin complexes of V(V) were prepared and isolated as solids of a color characteristic of the ligand with the general formulas;$[VO(Lom)_2DMF]Cl_3$, $[VO(Lom)_2An]Cl_3$, $[VO(Lom)_2o\text{-}Tol]Cl_3$, $[VO(Lom)_2Py]Cl_3$ and $[VO(Lom)_2Et_3N]Cl_3$. The prepared complexes are formed with a metal to ligand ratios amounting to 1:2:1 for all complexes. The new synthesized complexes were characterized with physicochemical and diverse spectroscopic techniques (IR, UV-Vis. and ^{1}H NMR spectroscopes) as well as thermal analysis. The found values of elemental analysis agree well with the calculated percentage of C, H, N and halogen and prove the molecular formulas of the prepared complexes.

Magnetic moment measurements were carried out at room temperature and the data indicated that the complexes of V(V) are found in diamagnetic character with molecular geometries octahedral. The molar conductivity values of free ligand and vanadium complexes in DMSO-d_6 as a solvent at 1.0×10^{-3} M were found at 20.0 - 310.00 S cm^2 mol^{-1}. The higher values of the complexes than that of the free lomefloxacin ligand indicated the formation of complexes and the complexes are electrolytes.

Table (1): Elemental analysis and physico-analytical data for lomefloxacin and its metal complexes

Compounds MWt. (M.F.)	Yield%	Mp/^{o}C	Color	Found (Calcd.) (%)					Λ (S cm^2 mol^{-1})
				C	H	N	M	Cl	
Lom	-	239	White	(58.12)	(5.41)	(11.97)			20
351 ($C_{17}H_{19}N_3O_3F_2$)				58.10	5.39	11.95	-	-	
$[VO(Lom)_2DMF]Cl_3$	95	268-270	Dark	(46.81)	(4.74)	(10.33)	(5.37)	(11.23)	283
948.44 ($VC_{37}H_{45}F_4N_7O_8Cl_3$)			green	46.80	4.73	10.22	5.37	11.22	
$[VO(Lom)_2An]Cl_3$	90	245-248	Black	(49.56)	(4.65)	(10.12)	(5.26)	(11.00)	307
968.44 ($VC_{40}H_{45}F_4N_7O_7Cl_3$)				49.53	4.63	10.10	5.25	10.99	
$[VO(Lom)_2o\text{-}Tol]Cl_3$	90	252-255	Black	(50.08)	(4.78)	(9.98)	(5.19)	(10.84)	298
982.44 ($VC_{41}H_{47}F_4N_7O_7Cl_3$)				49.92	4.76	9.95	5.17	10.82	
$[VO(Lom)_2Py]Cl_3$	85	280-283	Brown	(49.03)	(4.51)	(10.27)	(5.34)	(11.16)	290
954.44 ($VC_{39}H_{43}F_4N_7O_7Cl_3$)				48.97	4.48	10.24	5.33	11.14	
$[VO(Lom)_2Et_3N]Cl_3$	95	262-265	Yellow	(49.16)	(5.43)	(10.04)	(5.22)	(10.91)	310
976.44 ($VC_{40}H_{53}F_4N_7O_7Cl_3$)				49.13	5.41	10.01	5.18	10.88	

Infrared spectra

The infrared spectra of lomefloxacin and their complexes $[VO(Lom)_2DMF]Cl_3$, $[VO(Lom)_2An]Cl_3$, $[VO(Lom)_2o\text{-}Tol]Cl_3$, $[VO(Lom)_2Py]Cl_3$ and $[VO(Lom)_2Et_3N]Cl_3$ are usually similar, (Fig. 1). The absence of very strong absorption band at 1725 cm^{-1}, arising from the carboxylic group (COOH) for under investigation complexes, states that the hydrogen ion in the lomefloxacin molecule is substituted by the metal ion and the lomefloxacin is the coordinated ligand **[**6-9]. The stretching asymmetric (ν_{as}) of carboxylate group found between 1616and 1620 cm^{-1} and of the symmetric vibrations (ν_s) from 1389 to 1400cm^{-1}confirm these hypotheses.

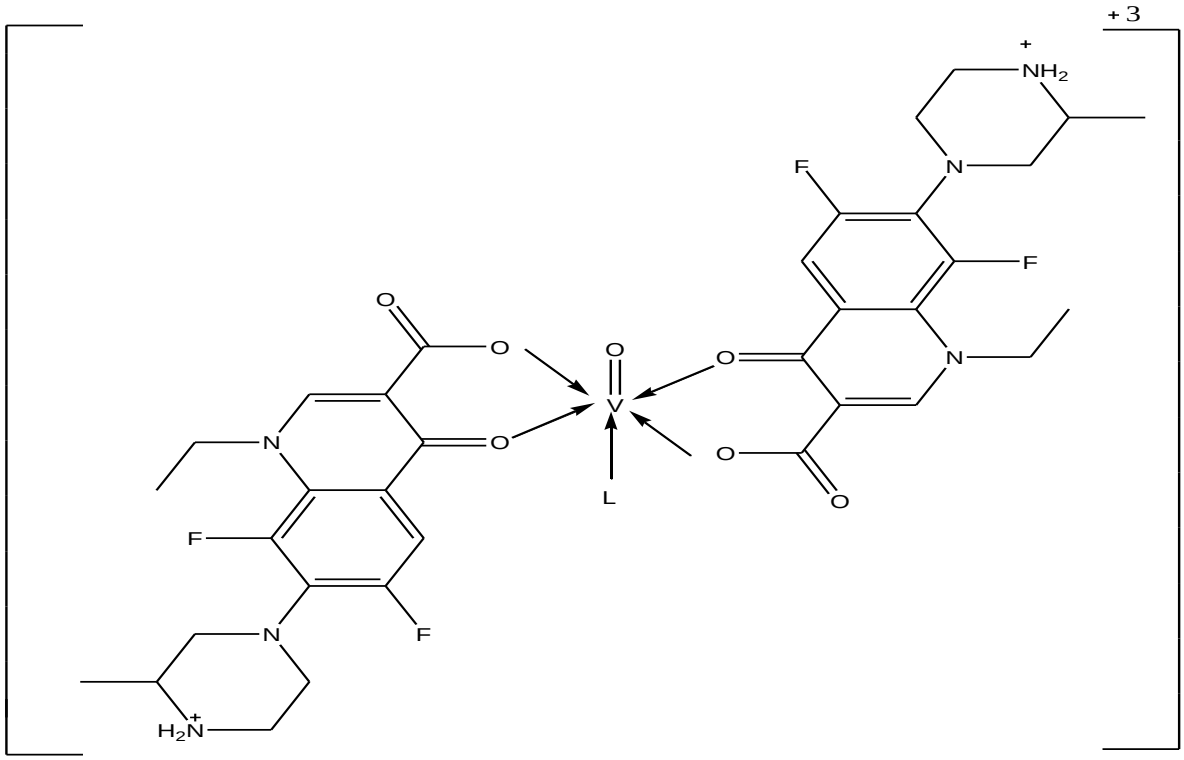
The band observed at 1618 cm^{-1} in the spectrum of the free lomefloxacin has been assigned before to the stretching vibration of the carbonyl group ν(C=O) **[**4, 6, 10-12]. The shift of the carbonyl group to a lower value, (Table 2), from 1618 cm^{-1} to 1533 cm^{-1} for $[VO(Lom)_2DMF]Cl_3$, to 1562 cm^{-1} for $[VO(Lom)_2An]Cl_3$, to 1589 cm^{-1} for $[VO(Lom)_2o\text{-}Tol]Cl_3$, to 1531 cm^{-1} for $[VO(Lom)_2Py]Cl_3$ and to 1558 cm^{-1} for $[VO(Lom)_2Et_3N]Cl_3$ indicates coordination of lomefloxacin through oxygen atom of the carbonyl group.

The stretching vibrations ν(C-H) of the phenyl, $–CH_2$ and $–CH_3$ groups in these complexes were observed in the region 3059- 2700 cm^{-1}. A group of weak to strong bands lying in the range 1254-1122 cm^{-1} could be assigned to the ν(C-O), ν(C-N) and ν(C-C) in all complexes. Also, the spectra of the isolated complexes showed a group of bands with different intensities which characteristics for ν(M-O) and ν(M-N). The ν(M-O) and ν(M-N) bands observed at 644, 489 and 444cm^{-1} for DMF, at 644, 583 and 475 cm^{-1} for An, at 656 and 575$cm^{-1}$for o-Tol, at 679 and 490cm^{-1} for Py, at 648, 559 and 455 cm^{-1} for Et_3N complexes .

The stretching vibration ν ($-NH_2^+$) observed in the spectra of free lomefloxacin and its complexes are at the same region, 2677-2444 cm^{-1}.The data given in Table 2 showed that ν(V=O) is a very strong band at 980 cm^{-1} also the infrared spectra of the prepared complexes display changes in the aromatic ring vibrations in comparison to the corresponding absorption bands for free ligand (Table 2).

According to the above discussion lomefloxacin is coordinated with the metal ion as bidentate ligand through oxygen atom of carbonyl and one oxygen atom of carboxylic group.

The proposed structure formula on the basis of the results discussed according to the infrared spectra located as follows (scheme 6).



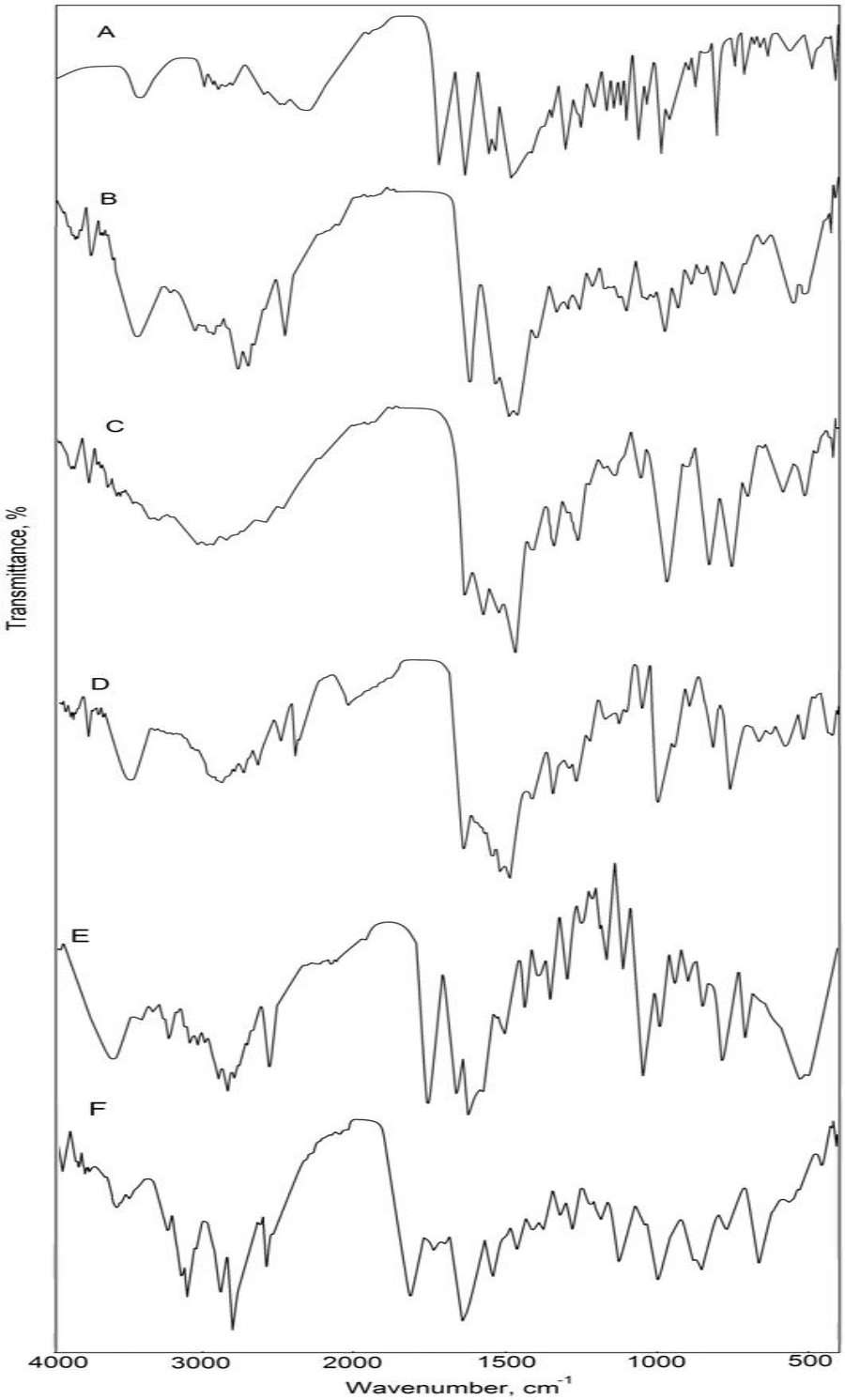
Scheme 1: The coordination mode of V(V) with lomefloxacin and L (L = DMF, An, Py, o-Tol and Et_3N)

Table (2): Infrared frequencies (cm^{-1}) and tentative assignments for (A) (Lom); (B) $[VO(Lom)_2DMF]Cl_3$, (C) $[VO(Lom)_2An]Cl_3$, (D) $[VO(Lom)_2oTol]Cl_3$, (E) $[VO(Lom)_2Py]Cl_3$ and (F) $[VO(Lom)_2Et_3N]Cl_3$.

A	B	C	D	E	F	Assignments
3438m,br	3433ms	3333w	3422ms	3440ms	3425w	ν(O-H); H_2O; COOH
3056m	3044m	3044vw	3044vw	3059ms	3055ms	ν(C-H); aromatic
2966vw 2933m 2890w 2845m 2757m 2701ms	2978sh 2936w 2893w 2867sh 2766 m 2704m	2978vw 2936w 2847w 2800vw 2755sh 2733sh	2955sh 2911vw 2889sh 2867w 2822sh 2778w 2704m	2936w 2885m 2844w 2758w 2700m	2974w 2939ms 2911w 2800sh 2746ms	ν(C-H); aliphatic
2661w 2635vw 2455s	2662ms 2600sh 2457s	2596w 2472w	2667sh 2611m 2457m	2662w 2588w 2556sh 2457vs	2677vs 2534w 2492ms 2444vw	ν($-NH_2^+$)
1725vs	-	-	-	-	-	ν(C=O); COOH
-	1616vs	1620ms	1616ms	1616vs	1620vs	$\nu_{as}(COO^-)$
1618vs 1526ms 1497s	1533m 1489m	1562s 1512m	1589vw 1578vw 1556vw 1533w	1531s 1493s	1558m 1528w	ν(C=O); phenyl breathing modes
1471w 1456vw 1413w	1462m	1458vs	1462s	1450s 1433vw	1474s 1456sh	-CH; deformations of CH_2
-	1396ms	1400ms	1393s	1389ms	1393s	$\nu_s(COO^-)$
1331s 1298vw	1331m 1292m	1327s	1327m 1289sh 1256w	1331s 1292m	1327ms 1288w	$\delta_b(-CH_2)$
1257ms 1208s 1166s	1254ms 1211m 1167vw 1144vw 1122vw	1250vs 1211m 1178w 1130m	1254m 1211m 1144sh 1122w	1254s 1207s 1169m 1130w	1254m 1207w 1173m	ν(C-O), ν(C-N) and ν(C-C)
1116m 1093ms 1043s 1014m	1103s 1044sh 1033w 1011w	1089sh 1045s 1011sh	1096m 1045s	1092vs 1045vs	1111w 1092ms 1038s 1011sh	$\delta_r(-CH_2)$
978w 930s 889s 850m 806ms	930s 887ms 833m 806s	891m 825vs	934ms 887m 810s	930s 887ms 849ms 806s	937s 900sh 833w 814s	-CH-bend; phenyl
-	976s	961vs	988vs	980vs	967w	ν (V=O)
739ms	745s	752vs	748vs	745vs	741ms	$\delta_b(COO^-)$
650m 550w 514m 480w	644m 552m 513m 489sh 444sh 421s	694m 644w 583m 513m 475w 421vs	689sh 656w 611w 575ms 513s 421m	679s 522w 490m	648vs 600sh 559w 522vw 455m	ν(M-O), ν(M-N); +ring deformation

Keys: s=strong, w=weak, v=very, m=medium, br=broad, sh=shoulder, ν=stretching, δ_b=bending

Figure 1: Infrared spectra for (A) (Lom); (B) $[VO(Lom)_2DMF]Cl_3$, (C) $[VO(Lom)_2An]Cl_3$, (D) $[VO(Lom)_2o\text{-}Tol]Cl_3$, (E) $[VO(Lom)_2Py]Cl_3$ and (F) $[VO(Lom)_2Et_3N]Cl_3$.



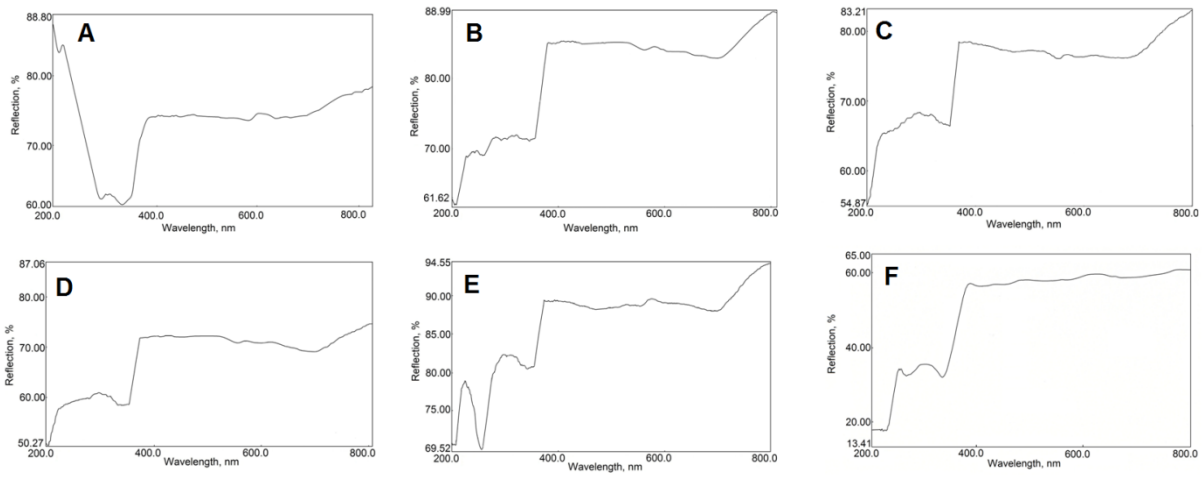
Electronic reflection spectra

The formation of the metal complexes was also confirmed by UV-Vis. spectra. Fig. 2 showed the electronic solid reflection spectra of free lomefloxacin and Table 3 reported the reflection spectra of lomefloxacin metal complexes from 800-200 nm. The reflection spectrum of free lomefloxacin showed bands at 214, 298 and 304 nm which is assigned to π-π* and n-π* transitions. For the five complexes the reflectance bands λ_{max} shifts to higher and to lower values attributed to complexation behavior of lomefloxacin towards metal ions.These complexes showed new band around 560 nm, which may be assigned to the ligand to metal charge-transfer [11, 12].

Table (3): UV-Vis. Spectra of (A)(Lom); (B) $[VO(Lom)_2DMF]Cl_3$,(C)$[VO(Lom)_2An]Cl_3$,(D)$[VO(Lom)_2o$-Tol$]Cl_3$,(E) $[VO(Lom)_2Py]Cl_3$and (F)$[VO(Lom)_2Et_3N]Cl_3$

Assignments (nm)	Lom	Lom complexes				
	A	B	C	D	E	F
π- π* transitions	214, 298	225,243, 253,279, 296	241,251, 296	273, 295	223, 295	220,226, 252,256
n- π* transitions	304	308,318, 371,408, 484	314,368, 387,398, 408, 447	400, 426	307,343, 376,388, 407, 421, 439	301,385, 436
Ligand-metal charge transfer	-	503,568	497,517, 566	497,504, 568	502,523, 535,541, 546,574	494,560

Figure 2: Electronic spectra of (A) (Lom); (B) $[VO(Lom)_2DMF]Cl_3$, (C) $[VO(Lom)_2An]Cl_3$, (D) $[VO(Lom)_2o$-Tol$]Cl_3$, (E) $[VO(Lom)_2Py]Cl_3$ and (F) $[VO(Lom)_2Et_3N]Cl_3$.



Thermal analysis

Thermogravimetric (TGA) and differential thermogravimetric (DTG) analyses were carried out for lomefloxacin and their isolated solid complexes $[VO(Lom)_2DMF]Cl_3$, $[VO(Lom)_2An]Cl_3$, $[VO(Lom)_2o$-Tol$]Cl_3$, $[VO(Lom)_2Py]Cl_3$ and $[VO(Lom)_2Et_3N]Cl_3$, under N_2 flow. Fig. 3 represented the TGA and DTG curves and Table 4 gives the maximum temperature values for decomposition along with the corresponding weight loss values for each step of the decomposition reaction. These data support the proposed complexes formulas. Lomefloxacin is thermally stable in the temperature range 25-250 ^oC. Decomposition of the lomefloxacin started at 250 ^oC and finished at 600 ^oC with one stage at two maxima 319 and 553 ^oC and is accompanied by a weight loss of 99.99% [13].

The lomefloxacinate of $[VO(Lom)_2DMF]Cl_3$ complex started at 50 ^oC and finished at 994^oC with two decomposition steps, the first stage with three maxima 60, 104 and 175 ^oC accompined by weight loss of 7.68% and may be attributed to the loss of DMF molecule [14] which is in good agreement with the calculated values of 7.70%. The

second stage with two maxima 294 and 419 ^{o}C accompained by weight loss of 73.45% which corresponds to loss of lomefloxacin molecules and giving the final product $0.5V_2O_5$+7C [15, 16].

The thermal decompostion of $[VO(Lom)_2An]Cl_3$ complex proceeds with two main degradation steps. The first stage of decomposition occurs at a temperature maximum of 158 ^{o}C. The found weight loss associated with step is 9.57% and may be attributed to the loss of an molecule which is in good agreement with the calculated values of 9.60%. The second stage of decomposition occurs at two maxima 308 and 415^{o}C and the weight loss found at this stage equals to 73.63%, giving $0.5V_2O_5$+6C as final product.

For $[VO(Lom)_2$o-Tol$]Cl_3$ complex the thermal decomposition exhibits two main degradation steps. The first step of decomposition occurs from 20 to204 ^{o}C at temperature maximum of 152 ^{o}C is accompanied by a weight loss of 10.90% in agreement with the theoretical values 10.89% for the loss of o-Tol molecule. The second step of decompostion occurs at three maxima 269, 396 and 507 ^{o}C with a weight loss of 75.23%, giving the final product $0.5V_2O_5$+4C.

The thermal decompostion of $[VO(Lom)_2Py]Cl_3$ complex the thermal decomposition exhibits two main degradation steps. The first step of decomposition occurs from 20 to 241 ^{o}C at temperature maximum of 129 ^{o}C is accompanied by a weight loss of 8.27% in agreement with the theoretical values 8.28% for the loss of Py molecule [14]. The second step of decompostion occurs at two maxima 356 and 517 ^{o}C with a weight loss of 73.40%, giving the final product $0.5V_2O_5$+7C.

The thermal decompostion of $[VO(Lom)_2Et_3N]Cl_3$ complex proceeds with two main degradation steps. The first stage of decomposition occurs at a temperature maximum of 168 ^{o}C. The found weight loss associated with step is 10.36% and may be attributed to the loss of Et_3N molecule [14] in agreement with the theoretical values 10.34%. The second stage of decomposition occurs at two maxima 286 and 582 ^{o}C and the weight loss found at this stage equals to 70.15%, giving the final product $0.5V_2O_5$+8C.

According to these conculsions, the decomposition mechansims proposed for lomfloxacin and thier complexes are summarized as follows:

(1) $C_{17}H_{19}N_3O_3F_2 \xrightarrow{319,\ 553\ ^{\circ}C} 6C_2H_2+3CO+C_2H_4+2HF+0.5H_2+1.5N_2$

(2) $[VO(C_{17}H_{19}N_3O_3F_2)_2(C_3H_7NO)]Cl_3 \xrightarrow{60,\ 104,\ 175\ ^{\circ}C} C_2H_6+CO+0.5N_2+0.5H_2+[VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3$

$[VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3 \xrightarrow{294,\ 419\ ^{\circ}C} 0.5V_2O_5+7C+13C_2H_2+CO+4HF+0.5H_2O+3HCl+NH_3+3NO+N_2+0.5H_2$

(3) $[VO(C_{17}H_{19}N_3O_3F_2)_2(C_6H_5NH_2)]Cl_3 \xrightarrow{158\ ^{\circ}C} 3C_2H_2+0.5N_2+0.5H_2+[VC_{34}H_{38}F_4N_6O_7Cl_3]$

$[VC_{34}H_{38}F_4N_6O_7Cl_3] \xrightarrow{308,\ 415\ ^{\circ}C} 0.5V_2O_5+6C+14C_2H_2+4HF+3HCl+0.5H_2O+2NO_2+2N_2+H_2$

(4) $[VO(C_{17}H_{19}N_3O_3F_2)_2(C_7H_9N)]Cl_3 \xrightarrow{152\ ^{\circ}C} 3.5C_2H_2+H_2+0.5N_2+ [VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3$

$[VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3 \xrightarrow{269,\ 396,\ 507\ ^{\circ}C} 0.5V_2O_5+4C+15C_2H_2+4HF+3HCl+0.5H_2O+4NO+N_2$

(5) $[VO(C_{17}H_{19}N_3O_3F_2)_2(C_5H_5N)]Cl_3 \xrightarrow{129\ ^{\circ}C} 2.5C_2H_2+ 0.5N_2+[VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3$

$[VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3 \xrightarrow{356,\ 517\ ^{\circ}C} 0.5V_2O_5+7C+13C_2H_2+CO+4HF+0.5H_2O+NH_3+3HCl+3NO+N_2+0.5H_2$

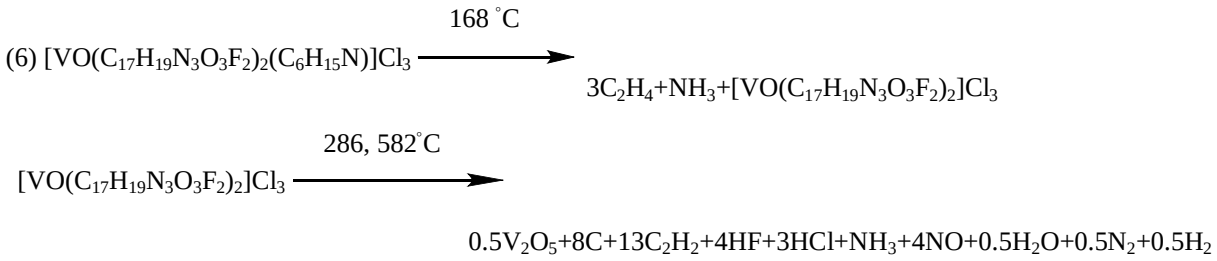
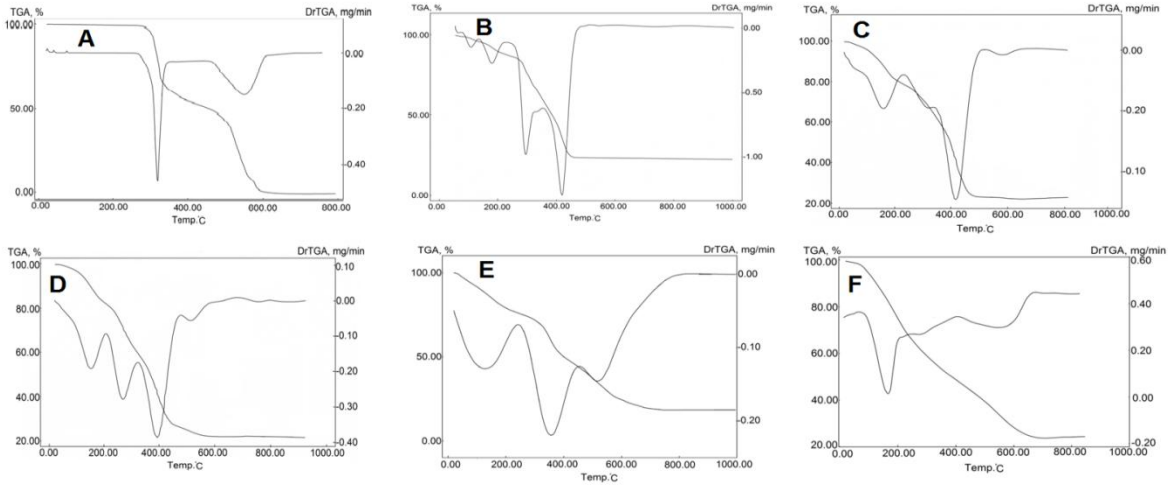

(6) $[VO(C_{17}H_{19}N_3O_3F_2)_2(C_6H_{15}N)]Cl_3$
168 °C
$3C_2H_4+NH_3+[VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3$
$[VO(C_{17}H_{19}N_3O_3F_2)_2]Cl_3$
286, 582°C
$0.5V_2O_5+8C+13C_2H_2+4HF+3HCl+NH_3+4NO+0.5H_2O+0.5N_2+0.5H_2$

Table (4): The maximum temperature T_{max}(°C) and weight loss values of the decomposition stages for LomandV(V) complexes

Compounds	Decomposition	T_{max}(°C)	Weight loss (%)		Lost species
			Calc.	Found	
Lom	First step	319, 553	100	99.99	$6C_2H_2+3CO+C_2H_4+2HF+0.5H_2+1.5N_2$
($C_{17}H_{19}N_3O_3F_2$)	Total loss		100,	100,	
	Residue		0.0	0.0	
$[VO(Lom)_2DMF]Cl_3$	First step	60, 104, 175	7.70	7.68	$C_2H_6+CO+0.5N_2+0.5H_2$
($VC_{37}H_{45}F_4N_7O_7Cl_3$)	Second step	294, 419	73.86	73.45	$13C_2H_2+CO+4HF+0.5H_2O+3HCl+NH_3+3NO+N_2+0.5H_2$
	Total loss		81.56	81.13	
	Residue		18.45	18.87	$0.5V_2O_5+7C$
$[VO(Lom)_2An]Cl_3$	First step	158	9.60	9.58	$3C_2H_2+0.5N_2+0.5H_2$
($VC_{40}H_{45}F_4N_7O_7Cl_3$)	Second step	308, 415	73.57	73.63	$14C_2H_2+4HF+3HCl+0.5H_2O+2NO_2+2N_2+H_2$
	Total loss		83.17	83.21	
	Residue		16.82	16.79	$0.5V_2O_5+6C$
$[VO(Lom)_2o\text{-}Tol]Cl_3$	First step	152	10.89	10.87	$3.5C_2H_2+H_2+0.5N_2$
($VC_{41}H_{47}F_4N_7O_7Cl_3$)	Second step	269, 396, 507	74.97	75.23	$15C_2H_2+4HF+3HCl+0.5H_2O+4NO+N_2$
	Total loss		85.86	86.10	
	Residue		14.14	13.90	$0.5V_2O_5+4C$
$[VO(Lom)_2Py]Cl_3$	First step	129	8.28	8.27	$2.5C_2H_2+ 0.5N_2$
($VC_{39}H_{43}F_4N_7O_7Cl_3$)	Second step	356, 517	73.39	73.40	$13C_2H_2+CO+4HF+0.5H_2O+NH_3+3HCl+3NO+N_2+0.5H_2$
	Total loss		81.63	81.67	
	Residue		18.37	18.33	$0.5V_2O_5+7C$
$[VO(Lom)_2.Et_3N]Cl_3$	First step	168	10.34	10.36	$3C_2H_4+NH_3$
($VC_{40}H_{53}F_4N_7O_7Cl_3$)	Second step	286,582	70.51	70.15	$13C_2H_2+4HF+3HCl+NH_3+4NO+0.5H_2O+0.5N_2+0.5H_2$
	Total loss		80.85	80.51	
	Residue		19.15	19.49	$0.5V_2O_5+8C$

Figure 3: TGA and DTG diagrams of (A) (Lom); (B) $[VO(Lom)_2DMF]Cl_3$, (C) $[VO(Lom)_2An]Cl_3$, (D) $[VO(Lom)_2o\text{-}Tol]Cl_3$, (E) $[VO(Lom)_2Py]Cl_3$ and (F) $[VO(Lom)_2Et_3N]Cl_3$.



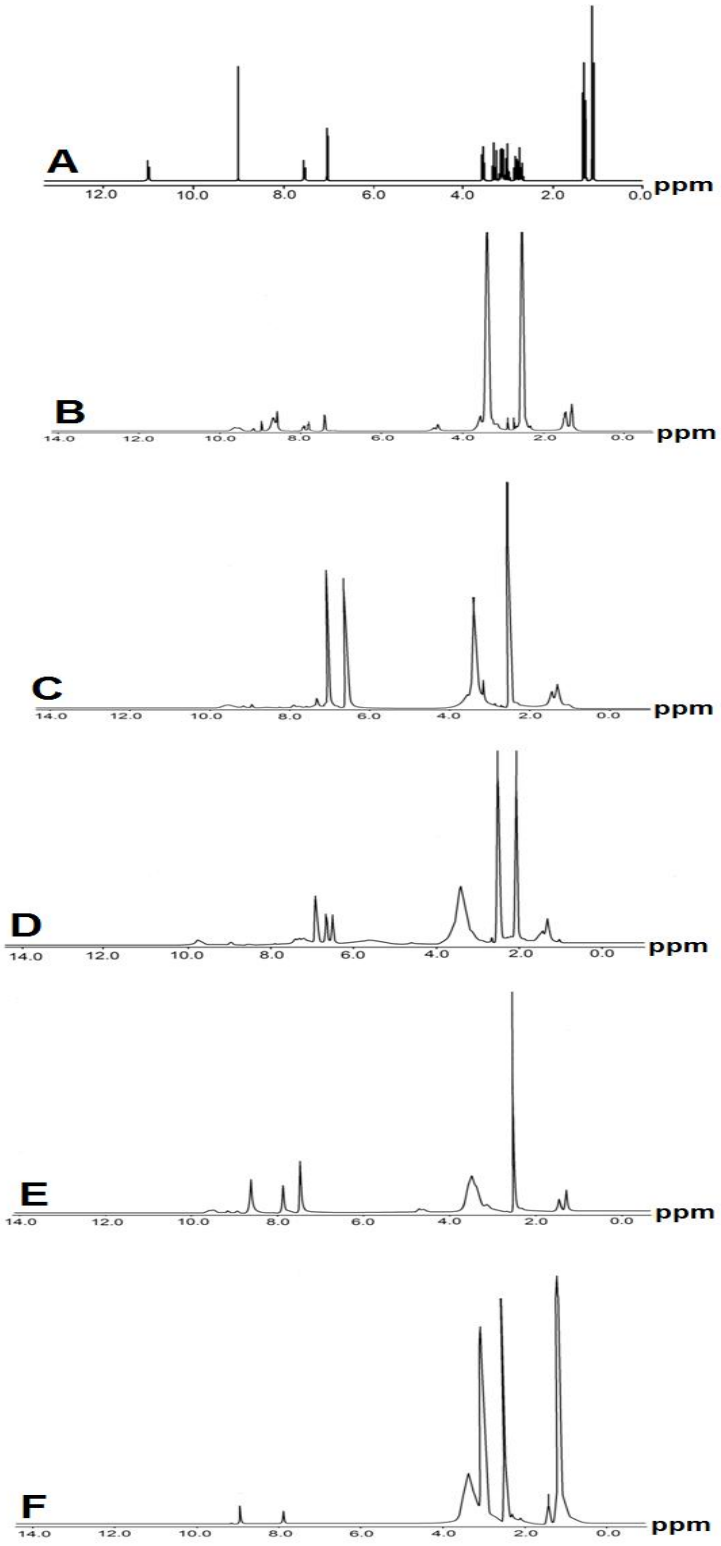
The ^{1}HNMR spectra

The ^{1}H NMR spectra presented the persuasive confirmationof the coordination modes. Thus, the ^{1}H NMR spectrua oflomefloxacin complexes on comparing with that of the free lomefloxacin indicated that lom acts as ligand through one of the oxygen atoms of the carboxylic group [17]. Fig. 4 showed the ^{1}H NMR spectra of the lomefloxacin and its complexes with V(V) which were carried out in DMSO-d_6 as a solvent. The data obtained are in agreement with the suggested coordination through the carboxylic group (absent the hydrogen signal of (COOH) in this case), and due to different chemical environments signals are recorded for the quaternized nitrogen ($-^+NH_2$). Table 5summarizes the assignments of ^{1}H NMR spectral data of free lom and its complexes.

Table (5): ^{1}H NMR values (ppm) and tentative assignments for (A) (Lom); (B) $[VO(Lom)_2DMF]Cl_3$, (C) $[VO(Lom)_2An]Cl_3$, (D) $[VO(Lom)_2o\text{-}Tol]Cl_3$ (E) $[VO(Lom)_2Py]Cl_3$ and (F)$[VO(Lom)_2Et_3N]Cl_3$

A	B	C	D	E	F	Assignments
1.31	1.28, 1.44	1.04, 1.30,1.44	1.04, 1.31,1.44	1.28, 1.46	1.16, 1.30,1.43	δH,-CH_3
3.51-3.61	2.32	2.32	2.05	2.32	2.12	δH, -NH
3.98	3.56	3.57	3.40	3.48	3.37	δH, -N-CH_2
7.47	7.39	7.00-7.32	7.18, 7.31,7.39	7.45	7.16	δH, -$^+NH_2$
8.95	7.77-9.24	7.56-9.53	7.72-9.19	7.86-9.28	7.86-9.16	δH, -CH_2 aromatic
11.00	-	-	-	-	-	δH, -COOH

Figure 4:^{1}H NMR spectra of (A) (Lom); (B) [VO(Lom)$_2$DMF]Cl$_3$, (C) [VO(Lom)$_2$An]Cl$_3$, (D) [VO(Lom)$_2$o-Tol]Cl$_3$, (E) [VO(Lom)$_2$Py]Cl$_3$ and (F) [VO(Lom)$_2$Et$_3$N]Cl$_3$.



Antimicrobial activity

The efficiencies of lomefloxacin and their metal complexes have been investigated against three Gram-negative, *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa* (*P. aeruginosa*) and *Klebsiella pneumonia* (K. pneumoniae) and three Gram-positive, *Staphylococcus aureus* (*S. aureus*), *Bacillis subtilis* (*B. subtilis*) and *Streptococcus pyogenes* (*S. pyogenes*) microorganisms. The results presented in Table 6 and Fig. 5.The results of the antibacterial study of the lomefloxacin and the five complexes (Table 6) have inhibitory action against all the three types of Gram-positive bacteria and Gram-negative bacteria. All complexes showed a good activity against Gram-negative and Gram-positive microorganisms than lomefloxacin and on the other hand, $[VO(Lom)_2$o-Tol$]Cl_3$ complex and $[VO(Lom)_2Et_3N]Cl_3$ exhibit excellent activity against all bacterial species when compared to the free lomefloxacin. Such increased activity of metal chelate can be explained on the basis of the overtone concept and chelation theory.

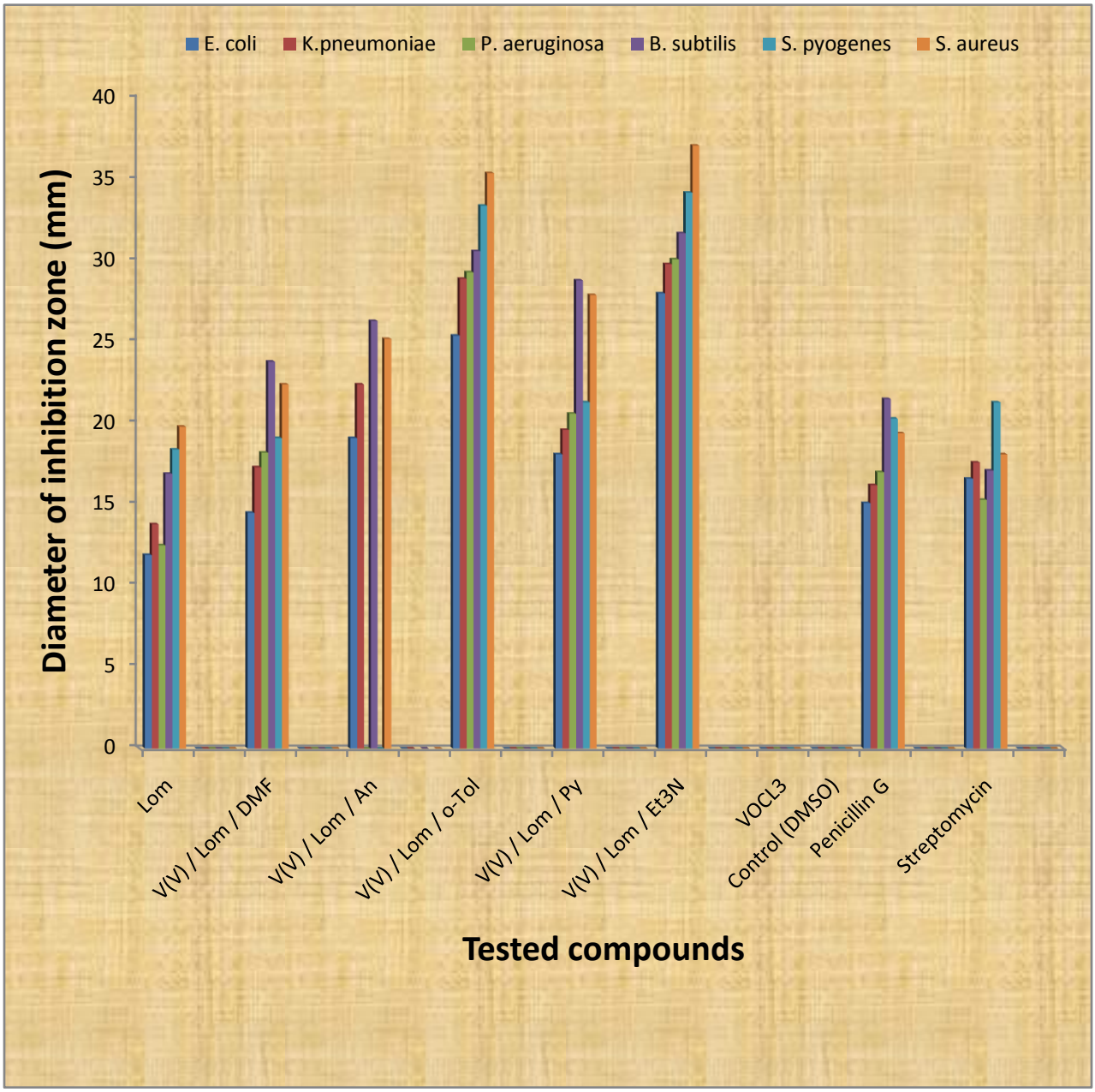
According to the overtone concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble materials in which liposolubility is an important factor that controls the antimicrobial activity. On chelation the polarity of the metal ion will be reduced to a greater extent due to overlap of ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further it increases the delocalization of π-electrons over the whole chelate ring and enhances the lipophilicity of the complexes [18]. This increased lipophilicity enhances the penetration of complexes into the lipid membranes and blocks the metal binding sites in enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the microorganisms [19-23].

Table (6): The inhibitation diameter zone values (mm) for Lom and their complexes.

compounds		Microbial Bacteria species					
		E. coli	*K.pneumoniae*	*P. aeruginosa*	*B. subtilis*	*S. pyogenes*	*S. aureus*
Lom		11.9 ±0.25	13.8 ±0.19	12.5 ±0.19	16.9 ±0.25	18.4 ±0.44	19.8 ±0.44
V(V)/Lom /DMF		14.5^{+1} ±0.05	17.3^{+1} ±0.1	18.2^{+1} ±0.04	23.8^{+2} ±0.09	19.1^{NS} ±0.08	22.4^{+1} ±0.03
V(V)/ Lom /An		19.1^{+1} ±0.06	22.4^{+2} ±0.06	NA	26.3^{+2} ±0.05	NA	25.2^{+1} ±0.3
V(V)/ Lom /o-Tol		25.4^{+2} ±0.1	28.9^{+3} ±0.08	29.3^{+3} ±0.02	30.6^{+3} ±0.03	33.4^{+3} ±0.1	35.4^{+3} ±0.05
V(V)/ Lom /Py		18.1^{+1} ±0.07	19.6^{+1} ±0.05	20.6^{+2} ±0.2	28.8^{+3} ±0.03	21.3^{+1} ±0.09	27.9^{+2} ±0.3
V(V)/ Lom /Et_3N		28.0^{+3} ±0.1	29.8^{+3} ±0.1	30.1^{+3} ±0.5	31.7^{+3} ±0.5	34.2^{+3} ±0.4	37.1^{+3} ±0.5
$VOCl_3$		0	0	0	0	0	0
Control (DMSO)		0	0	0	0	0	0
standard	Penicillin G	15.1 ±0.07	16.2 ±0.09	17.0 ±0.05	21.5 ±0.06	20.3 ±0.2	19.4 ±0.08
	Streptomycin	16.6 ±0.04	17.6 ±0.09	15.3 ±0.08	17.1 ±0.04	21.3 ±0.2	18.1 ±0.08

NA: No activity, data are expressed in the form of mean ± SD.Statistical significance $^{(NS)}$ not significance, $p > 0.05$; $^{(+1)}$ significant, $p < 0.05$; $^{(+2)}$ highly significant, $p < 0.01$; $^{(+3)}$ very highly significant , $p < 0.001$; student's t-test.

Figure 5: Statistical representation for biological activity of lomefloxacin and its complexes.



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