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Report on oxovanadium (IV) complexes of ciprofloxacin and their characterization by IR spectroscopy and their potentiometric study

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Abstract

The reaction between ciprofloxacin and $VOSO_4.3H_2O$ in 1:1, 1:2 and 1:3 molar ratio in methanol was investigated at 20˚C, 0˚C and -10˚C. In various pH conditions the different complexes which are formulated as $VO(H_2O)_3L$, $VO(H_2O)L_2$ and VL_3 have been formed by titration of $VOSO_4.3H_2O$ with ciprofloxacin in the presence of NaOH. These complexes have been characterized by IR spectroscopy. The order of stability is estimated as 1:1 >1:3 >1:2 which is justified by the proposed mechanism.

Keywords: Oxovanadium(IV) esters, IR, potentiometric study, stability constant.

INTRODUCTION

Many organic compounds used in medicine not have purely organic mode of their action, some of them are activated or bio transferred by metal ions. Metallic elements play crucial role in biological systems

Metals such as copper, zinc, iron and manganese are incorporated into catalytic proteins, the metalloenzymes, which facilitate chemical reaction needed for life (Holm and Solomn, 1996).

Vanadium trioxide (V_2O_3) is basic in solution and dissolves in acids to give the green hexa- aquo ion, $V(H_2O)_6^{3+}$. In solution, V^{3+} is a strong reducing agent and slowly attacks water with the production of hydrogen. Vanadium is usually bound to oxygen as a negatively charged polymeric oxyanion that tends to complex to polarizable ligands, such as phosphorus and sulfur. Vanadium has good structural strength and a low fission neutron cross section, making it useful in nuclear applications (Lee, 1996). This ion dominates vanadium(IV) chemistry. It is obtained by mild reduction of the VO_2^+ or by air-oxidation of V^{III} solutions.

The interaction of V_2O_5 with ethanolic HCl gives a solution containing $VOCl_5^{3-}$ that can conveniently be need as a source of V^{IV} oxo complexes (Cotton et al., 1999).

$VO^{2+} + 2H^+ + e^-$ $V^{3+} + H_2O$ $E^0 + 0.34$ V

$VO_2^+ + 2H^+ + e$ $VO^{2+} + H_2O$ $E^0 + 1.0$

Vanadium is a powerful alloying agent; a small amount adds strength, toughness and heat resistance. Vanadium-aluminum-titanium alloys are used in high-speed airframes and jet engines.

They are used as catalytic converters for the exhaust gases of internal combustion engines. Vanadium compounds are used as mordants in the dyeing and printing of fabrics, particularly for fixing aniline black on silk (in form of ammonium vanadates) and cathode-ray tubes.

We are reporting here the oxovanadium(IV) complexes of ciprofloxacin (Figure 1) and their characterization by IR spectroscopy and their potentiometric study.

EXPERIMENTAL

MATERIALS

$VOSO_4.3H_2O$ (Aldrich 99% purity) was used as received. Distilled water was used for the preparation of 0.2 M NaOH solution. While the methanol was used as a solvent for the preparation of 0.01M solution of vanadyl sulphate trihydrate and 0.01 M solution of ciprofloxacin. pH meter (Hanna HI 9024, Aldrich) was calibrated by using the buffer tablet of pH 4.

General procedure

Preparation of solution for different molar ratios

For potentiometric titration, 1:1, 1:2 and 1:3 molar ratios were prepared by mixing 25 mL of 0.01 M $VOSO_4.3H_2O$ solutions with 25, 50 and 75 mL of 0.01M solution of ciprofloxacin in volumetric flask.

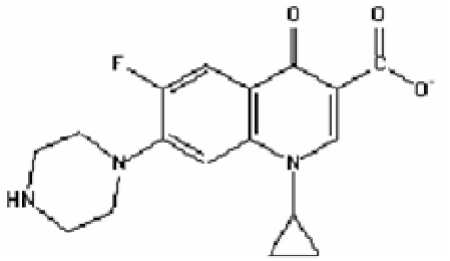

Figure 1. Chemical structure ofCiprofloxacin.

Table 1. Physical parameters of oxovanadium(IV) esters.

Comp. No.	General Formula	Molar Ratio	M.W.	m.p (˚C)
1	$[VO(H_2O)_3L]$	1:1	451	284
2	$[VO(H_2O)L_2]$	1:2	745	231
3	$[VL_3]$	1:3	1041	298

Conditions

The titrations were carried out at 20, 0 and -10^{o}C with standard 0.2 M NaOH. The 20^{o}C was room temperature, while 0 and -10^{o}C were maintained by keeping the titration flask in ice and ice-salt bath, respectively.

Titration procedure

The reaction mixtures were stirred on a magnetic stirrer while the titrations were carried out and pH were measured after every 0.2 mL addition of NaOH solution. For all three molar ratios, first addition of NaOH solution cause color change of the solutions with turbidity, which means that complexation started. At the end of the reactions all solution became clear and white precipitates of Na_2SO_4 formed (Shahzadi and Ali, 2005). These precipitates were filtered and solvents were evaporated at room temperature. Green colored solid products obtained were recrystallized in choroform: petroleum ether (1:1).

RESULTS AND DISCUSSION

Physical data for the reported compounds are given in Table 1 and are soluble in common organic solvents e.g., chloroform, *n*-hexane (Aldrich) etc and have a sharp melting point.

The potentiometric titration curves for 1:1, 1:2 and 1:3 M/L ratios are given in Figure 2. These figures shows that titration curves of VO(IV) complexes at different temperature found to have less depression but more twist which showed the low stability constants values with more species present at a time. The log β values are given in Table 2 and these (log β) values show that order of the stability would be 1:1 > 1:3 > 1:2 M/L molar ratio. pH titration data for 1:1, 1:2 and 1:3 M/L ratios at 20, 0 and -10^{o}C are given in Tables 3 - 5, respectively.

Mechanism involved

Following reactions were proposed in the formation of the complexes at different molar ratios.

$$[VO(H_2O)_5]^{2+} + HL \rightleftharpoons [VO(H_2O)_3L]^{+} + H^{+} + 2H_2O \quad (i)$$

$$[VO(H_2O)_3L]^{+} + 2HL \rightleftharpoons [VO(H_2O)L] + 2H^{+} + 2H_2O \quad (ii)$$

OR

$$[VO(H_2O)L_2] + HL \rightleftharpoons [VL_3]^{+} + \bar{O}H + H_2O \quad (iii)$$

$$[VO(H_2O)_5] + 3HL \rightleftharpoons [VL_3]^{+} + \bar{O}H + 3H_2O \quad (iv)$$

i) Equation (i) and (iv) shows that in case of 1:1 and 1:3, the degree of hydrolysis is same or entropy should be same. Reason is that in both reactions only one H^{+} is produced.
ii) According to equation (ii) and (iii), both type of mechanism are possible for 1:2 M/L ratio. Equation (ii) shows that entropy of 1:1 and 1:2 complexes should be same but in case of second mechanism as given in equation (iii) entropy should be in negative value.

This means that stability of 1:2 complex is less than 1:3 which is less than 1:1. We can show the stability order as 1:1 > 1:3 > 1:2

Stability of 1:3 complexes is greater than 1:2 due to removal of vanadyl oxygen during the formation of 6-coordinated complex from simple bidentate ligand (Otieno, 2003; Yalcin et al., 1998).

Proposed structure

Proposed structures for the complexes are given as Figure 3. These structures show that ligand acts as bidentate in these complexes and 6-coordinated complexes are obtained.

IR spectral data

The infrared spectra (Bio-Rad Elmer 16 FPC FT-IR instrument) were recorded as KBr discs, in the range 4000-400 cm^{-1}. The spectra of the oxovanadium (IV) complexes show narrow bands of medium intensity in the range 950 - 987 cm^{-1} due to the V=O stretching vibration. The complexation of the oxovanadium(IV) cation with the ligand is confirmed by the disappearance of –OH band occurring at 2500-3000 cm^{-1} in the ligand, which is characteristic of carboxylic acids. The peak for ν(COO) in the region 1712-1745 cm^{-1} has been shifted to the lower frequency, which confirm complexation. The lowering of ν_{asym}(COO) and rise in ν_{sym}(COO) the [= ($_{asym}$-$_{sym}$)] show bidentate nature of ligands in all the complexes which is in the range 189 - 230 cm^{-1}. This value is higher for the ligands. A decrease in the stretching vibration for ν(V=O) from the normal value (980 cm^{-1}) for all the complexes, show an electron transfer from ligand to the

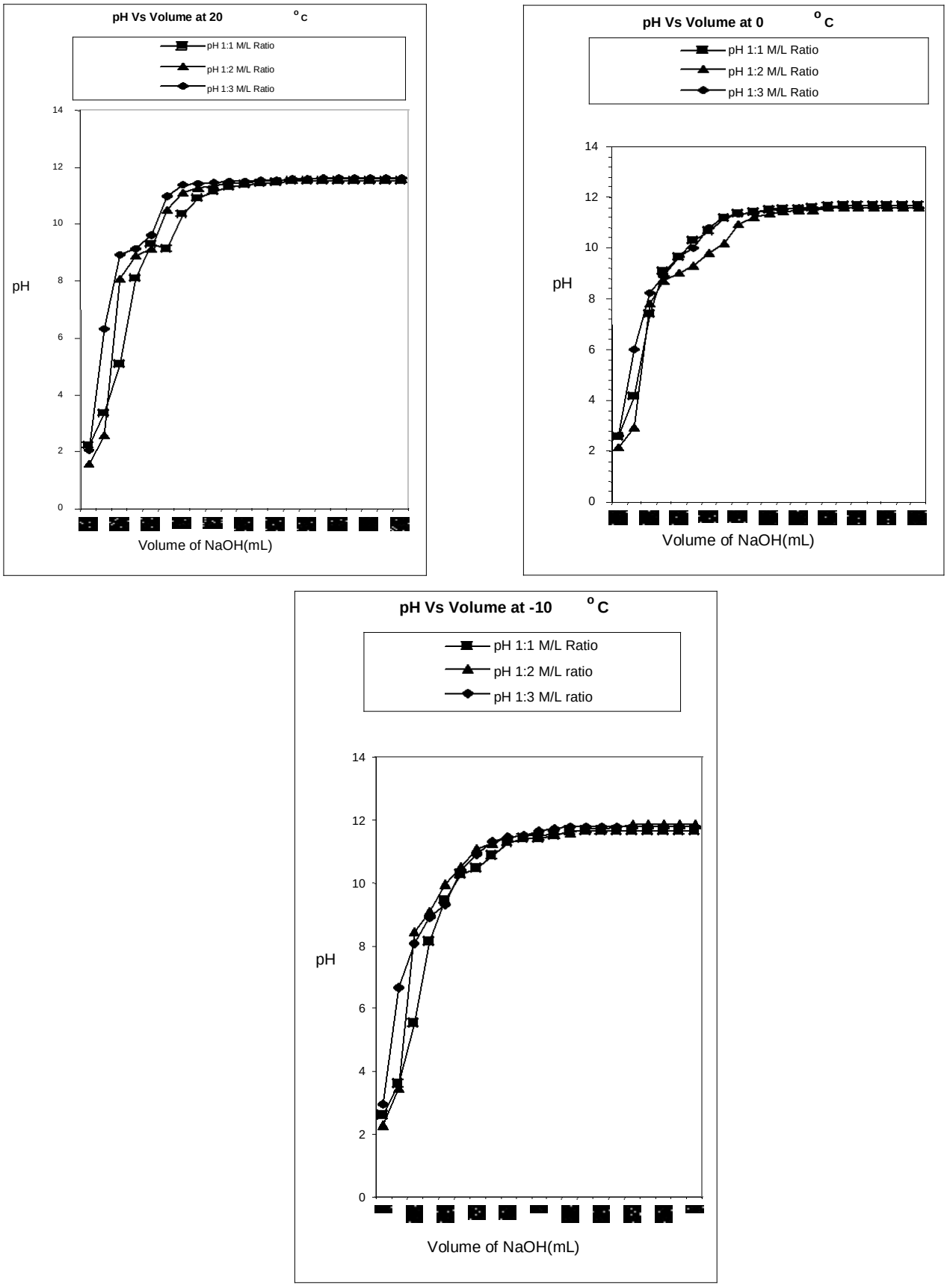

Figure 2. Potentiometric titration curves for 1:1, 1:2 and 1:3 M/L ratios.

Table 2. Stability constant data for oxovanadium(IV) complexes of ciprofloxacin.

Complex	Temperature (^{o}C)	M/L Ratio	log β
VO(IV)-Cipro[a]	20	1:1	3.30
		1:2	5.50
		1:3	7.60
VO(IV)-Cipro[a]	0	1:1	3.18
		1:2	5.32
		1:3	7.45
VO(IV)-Cipro[a]	-10	1:1	3.06
		1:2	5.20
		1:3	7.30

[a]Cipro = Ciprofloxacin

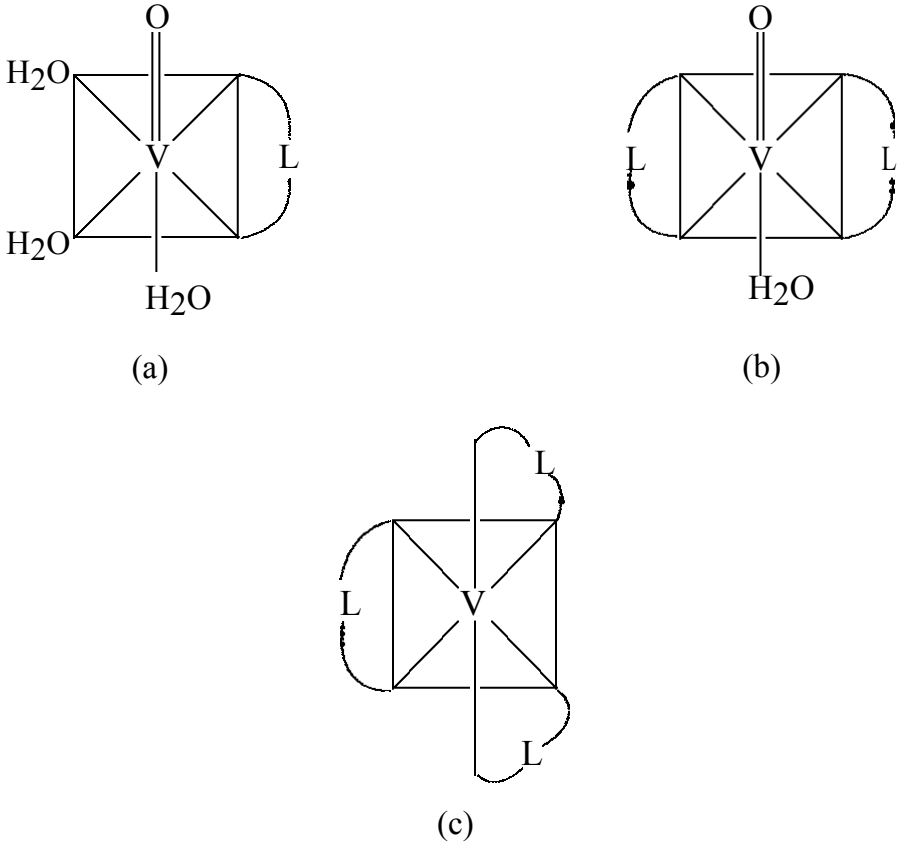

Figure 3. Proposed structures of oxovanadium(IV) esters in (a) 1:1 (b) 1:2 and (c) 1:3.

metal. It may be due to H_2O molecule attached to metal. Its presence is shown by ν(O–H) stretch observed above 3450 cm^{-1} for complexes.

Conclusion

Potentiometric study has been carried out between ciprofloxacin and $VOSO_4.3H_2O$ in 1:1, 1:2 and 1:3 molar ratio in methanol at 20, 0 and - 10˚C. In various pH conditions the different complexes which are formulated as $VO(H_2O)L_2$ and VL_3 have been formed by titration of $VOSO_4.3H_2O$ with ciprofloxacin in the presence of NaOH to measure the stabilities of complexes and characterized by IR; and hence give an insight into its possible role in binding metal ions. Pka values are determined for 1:1, 1:2 and 1:3 M/L ratio at different temperatures, which show that end points of the titration are sharp. The order

Table 3. pH titration data for 1:1, 1:2 and 1:3 M/L ratios at 0°C.

Volume of NaOHadded(mL)	pH 1:1M/L Ratio	[H+]=antilog(- pH)	$K_a=[H^+][L^-]/[HL]$	$pK_a=-\log K_a$	pH 1:2 M/L Ratio	[H+]=antilog(- pH)	$K_a=[H^+][L^-]/[HL]$	$pK_a=-\log K_a$	pH 1:3 M/L Ratio	[H+]=antilog(- pH)	$K_aH[L]=[H^+][L^-]$	$pK_a=-\log K_a$
0.0	2.58	2.63E-03	6.92E-04	3.16	2.16	6.92E-03	4.79E-03	2.32	2.6	2.51E-03	6.31E-04	3.2
0.2	4.12	7.59E-05	5.75E-07	6.24	2.91	1.23E-03	1.51E-04	3.82	6.02	9.55E-07	9.12E-11	10
0.4	7.41	3.89E-08	1.51E-13	12.8	7.81	1.55E-08	2.40E-14	13.6	8.23	5.89E-09	3.47E-15	14.5
0.6	9.05	8.91E-10	7.94E-17	16.1	8.72	1.91E-09	3.63E-16	15.4	8.89	1.29E-09	1.66E-16	15.8
0.8	9.65	2.24E-10	5.01E-18	17.3	9.01	9.77E-10	9.55E-17	16	9.66	2.19E-10	4.79E-18	17.3
1.0	10.28	5.25E-11	2.75E-19	18.6	9.28	5.25E-10	2.75E-17	16.6	10.02	9.55E-11	9.12E-19	18
1.2	10.67	2.14E-11	4.57E-20	19.3	9.82	1.51E-10	2.29E-18	17.6	10.78	1.66E-11	2.75E-20	19.6
1.4	11.17	6.76E-12	4.57E-21	20.3	10.2	6.31E-11	3.98E-19	18.4	11.22	6.03E-12	3.63E-21	20.4
1.6	11.34	4.57E-12	2.09E-21	20.7	10.92	1.20E-11	1.45E-20	19.8	11.34	4.57E-12	2.09E-21	20.7
1.8	11.41	3.89E-12	1.51E-21	20.8	11.22	6.03E-12	3.63E-21	20.4	11.41	3.89E-12	1.51E-21	20.8
2.0	11.51	3.09E-12	9.55E-22	21	11.36	4.37E-12	1.91E-21	20.7	11.52	3.02E-12	9.12E-22	21
2.2	11.52	3.02E-12	9.12E-22	21	11.43	3.72E-12	1.38E-21	20.9	11.54	2.88E-12	8.32E-22	21.1
2.4	11.53	2.95E-12	8.71E-22	21.1	11.49	3.24E-12	1.05E-21	21	11.58	2.63E-12	6.92E-22	21.2
2.6	11.58	2.63E-12	6.92E-22	21.2	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2
2.8	11.63	2.34E-12	5.50E-22	21.3	11.59	2.57E-12	6.61E-22	21.2	11.6	2.51E-12	6.31E-22	21.2
3.0	11.68	2.09E-12	4.37E-22	21.4	11.59	2.57E-12	6.61E-22	21.2	11.6	2.51E-12	6.31E-22	21.2
3.2	11.68	2.09E-12	4.37E-22	21.4	11.59	2.57E-12	6.61E-22	21.2	11.6	2.51E-12	6.31E-22	21.2
3.4	11.68	2.09E-12	4.37E-22	21.4	11.59	2.57E-12	6.61E-22	21.2	11.6	2.51E-12	6.31E-22	21.2
3.6	11.68	2.09E-12	4.37E-22	21.4	11.59	2.57E-12	6.61E-22	21.2	11.6	2.51E-12	6.31E-22	21.2
3.8	11.68	2.09E-12	4.37E-22	21.4	11.59	2.57E-12	6.61E-22	21.2	11.6	2.51E-12	6.31E-22	21.2
4.0	11.68	2.09E-12	4.37E-22	21.4	11.59	2.57E-12	6.61E-22	21.2	11.6	2.51E-12	6.31E-22	21.2

Table 4. pH titration data for 1:1, 1:2 and 1:3 M/L ratios at 20°C.

Volume of NaOHadded(mL)	pH 1:1M/L Ratio	[H+]=antilog(- pH)	$K_a=[H^+][L^-]/[HL]$	$pK_a=-\log K_a$	pH 1:2 M/L Ratio	[H+]=antilog(- pH)	$K_a=[H^+][L^-]/[HL]$	$pK_a=-\log K_a$	pH 1:3 M/L Ratio	[H+]=antilog(- pH)	$K_a=[H^+][L^-]/[HL]$	$pK_a=-\log K_a$
0.0	2.23	5.89E-03	3.47E-03	2.46	1.58	2.63E-02	6.92E-02	1.16	2.07	8.51E-03	7.24E-03	2.14
0.2	3.35	4.47E-04	2.00E-05	4.7	2.57	2.69E-03	7.24E-04	3.14	6.31	4.90E-07	2.40E-11	10.6
0.4	5.06	8.71E-06	7.59E-09	8.12	8.08	8.32E-09	6.92E-15	14.2	8.94	1.15E-09	1.32E-16	15.9
0.6	8.08	8.32E-09	6.92E-15	14.2	8.91	1.23E-09	1.51E-16	15.8	9.12	7.59E-10	5.75E-17	16.2
0.8	9.29	5.13E-10	2.63E-17	16.6	9.12	7.59E-10	5.75E-17	16.2	9.63	2.34E-10	5.50E-18	17.3
1.0	9.12	7.59E-10	5.75E-17	16.2	10.51	3.09E-11	9.55E-20	19	10.99	1.02E-11	1.05E-20	20
1.2	10.35	4.47E-11	2.00E-19	18.7	11.12	7.59E-12	5.75E-21	20.2	11.39	4.07E-12	1.66E-21	20.8
1.4	10.92	1.20E-11	1.45E-20	19.8	11.25	5.62E-12	3.16E-21	20.5	11.42	3.80E-12	1.45E-21	20.8
1.6	11.16	6.92E-12	4.79E-21	20.3	11.35	4.47E-12	2.00E-21	20.7	11.47	3.39E-12	1.15E-21	20.9
1.8	11.3	5.01E-12	2.51E-21	20.6	11.41	3.89E-12	1.51E-21	20.8	11.49	3.24E-12	1.05E-21	21
2.0	11.39	4.07E-12	1.66E-21	20.8	11.47	3.39E-12	1.15E-21	20.9	11.52	3.02E-12	9.12E-22	21
2.2	11.42	3.80E-12	1.45E-21	20.8	11.51	3.09E-12	9.55E-22	21	11.54	2.88E-12	8.32E-22	21.1
2.4	11.47	3.39E-12	1.15E-21	20.9	11.53	2.95E-12	8.71E-22	21.1	11.54	2.88E-12	8.32E-22	21.1
2.6	11.51	3.09E-12	9.55E-22	21	11.54	2.88E-12	8.32E-22	21.1	11.58	2.63E-12	6.92E-22	21.2
2.8	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2	11.59	2.57E-12	6.61E-22	21.2
3.0	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2	11.62	2.40E-12	5.75E-22	21.2
3.2	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2	11.62	2.40E-12	5.75E-22	21.2

Table 4. contd.

3.4	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2	11.62	2.40E-12	5.75E-22	21.2
3.6	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2	11.62	2.40E-12	5.75E-22	21.2
3.8	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2	11.62	2.40E-12	5.75E-22	21.2
4.0	11.51	3.09E-12	9.55E-22	21	11.59	2.57E-12	6.61E-22	21.2	11.62	2.40E-12	5.75E-22	21.2

Table 5. pH titration data for 1:1, 1:2 and 1:3 M/L ratios at -10°C.

Volume of NaOHadded(mL)	pH 1:1M/L Ratio				pH 1:2 M/L Ratio				pH 1:3 M/L Ratio			
		pH)	$K_a = [H][L]/[HL]$	$pK_a = -\log K_a$		pH)	$K_a = [H][L]/[HL]$	$pK_a = -\log K_a$		pH)	$K_a = [H][L]/[HL]$	$pK_a = -\log K_a$
0.0	2.61	2.45E-03	6.03E-04	3.22	2.29	5.13E-03	2.63E-03	2.58	2.95	1.12E-03	1.26E-04	3.9
0.2	3.6	2.51E-04	6.31E-06	5.2	3.46	3.47E-04	1.20E-05	4.92	6.64	2.29E-07	5.25E-12	11.3
0.4	5.5	3.16E-06	1.00E-09	9	8.43	3.72E-09	1.38E-15	14.9	8.07	8.51E-09	7.24E-15	14.1
0.6	8.13	7.41E-09	5.50E-15	14.3	9.08	8.32E-10	6.92E-17	16.2	8.88	1.32E-09	1.74E-16	15.8
0.8	9.43	3.72E-10	1.38E-17	16.9	9.94	1.15E-10	1.32E-18	17.9	9.31	4.90E-10	2.40E-17	16.6
1.0	10.25	5.62E-11	3.16E-19	18.5	10.5	3.16E-11	1.00E-19	19	10.39	4.07E-11	1.66E-19	18.8
1.2	10.46	3.47E-11	1.20E-19	18.9	11.08	8.32E-12	6.92E-21	20.2	10.92	1.20E-11	1.45E-20	19.8
1.4	10.87	1.35E-11	1.82E-20	19.7	11.27	5.37E-12	2.88E-21	20.5	11.32	4.79E-12	2.29E-21	20.6
1.6	11.27	5.37E-12	2.88E-21	20.5	11.46	3.47E-12	1.20E-21	20.9	11.44	3.63E-12	1.32E-21	20.9
1.8	11.42	3.80E-12	1.45E-21	20.8	11.51	3.09E-12	9.55E-22	21	11.48	3.31E-12	1.10E-21	21
2.0	11.42	3.80E-12	1.45E-21	20.8	11.51	3.09E-12	9.55E-22	21	11.65	2.24E-12	5.01E-22	21.3
2.2	11.51	3.09E-12	9.55E-22	21	11.54	2.88E-12	8.32E-22	21.1	11.7	2.00E-12	3.98E-22	21.4
2.4	11.64	2.29E-12	5.25E-22	21.3	11.59	2.57E-12	6.61E-22	21.2	11.77	1.70E-12	2.88E-22	21.5
2.6	11.64	2.29E-12	5.25E-22	21.3	11.7	2.00E-12	3.98E-22	21.4	11.77	1.70E-12	2.88E-22	21.5
2.8	11.64	2.29E-12	5.25E-22	21.3	11.72	1.91E-12	3.63E-22	21.4	11.77	1.70E-12	2.88E-22	21.5
3.0	11.64	2.29E-12	5.25E-22	21.3	11.77	1.70E-12	2.88E-22	21.5	11.77	1.70E-12	2.88E-22	21.5
3.2	11.64	2.29E-12	5.25E-22	21.3	11.85	1.41E-12	2.00E-22	21.7	11.77	1.70E-12	2.88E-22	21.5
3.4	11.64	2.29E-12	5.25E-22	21.3	11.85	1.41E-12	2.00E-22	21.7	11.77	1.70E-12	2.88E-22	21.5
3.6	11.64	2.29E-12	5.25E-22	21.3	11.85	1.41E-12	2.00E-22	21.7	11.77	1.70E-12	2.88E-22	21.5
3.8	11.64	2.29E-12	5.25E-22	21.3	11.85	1.41E-12	2.00E-22	21.7	11.77	1.70E-12	2.88E-22	21.5
4.0	11.64	2.29E-12	5.25E-22	21.3	11.85	1.41E-12	2.00E-22	21.7	11.77	1.70E-12	2.88E-22	21.5

of the stability is 1:1 > 1:3 > 1:2 which is justified with proposed mechanism. IR data show that ciprofloxacin are acts as bidentate ligand and 6-coordinated complexes obtained for 1:1, 1:2 and 1:3 M/L ratios

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