# Supplementary Materials

# Novel Enrofloxacin Schiff base metal complexes: Synthesis, spectroscopic characterization, computational simulation and antimicrobial investigation against some food and phyto-pathogens

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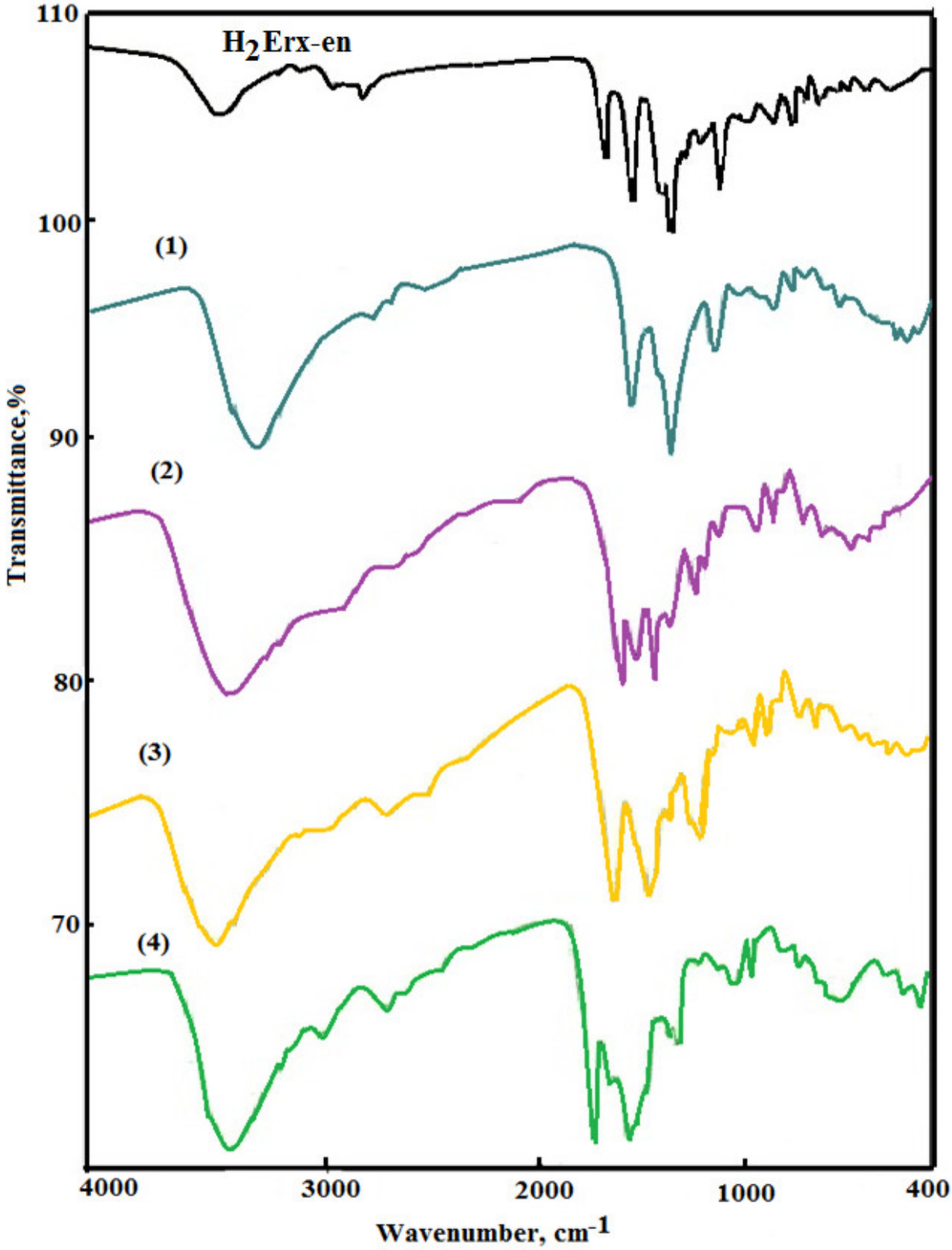



**Figure S1.** Infrared spectra for **$H_2$Erx-en** and its metal complexes

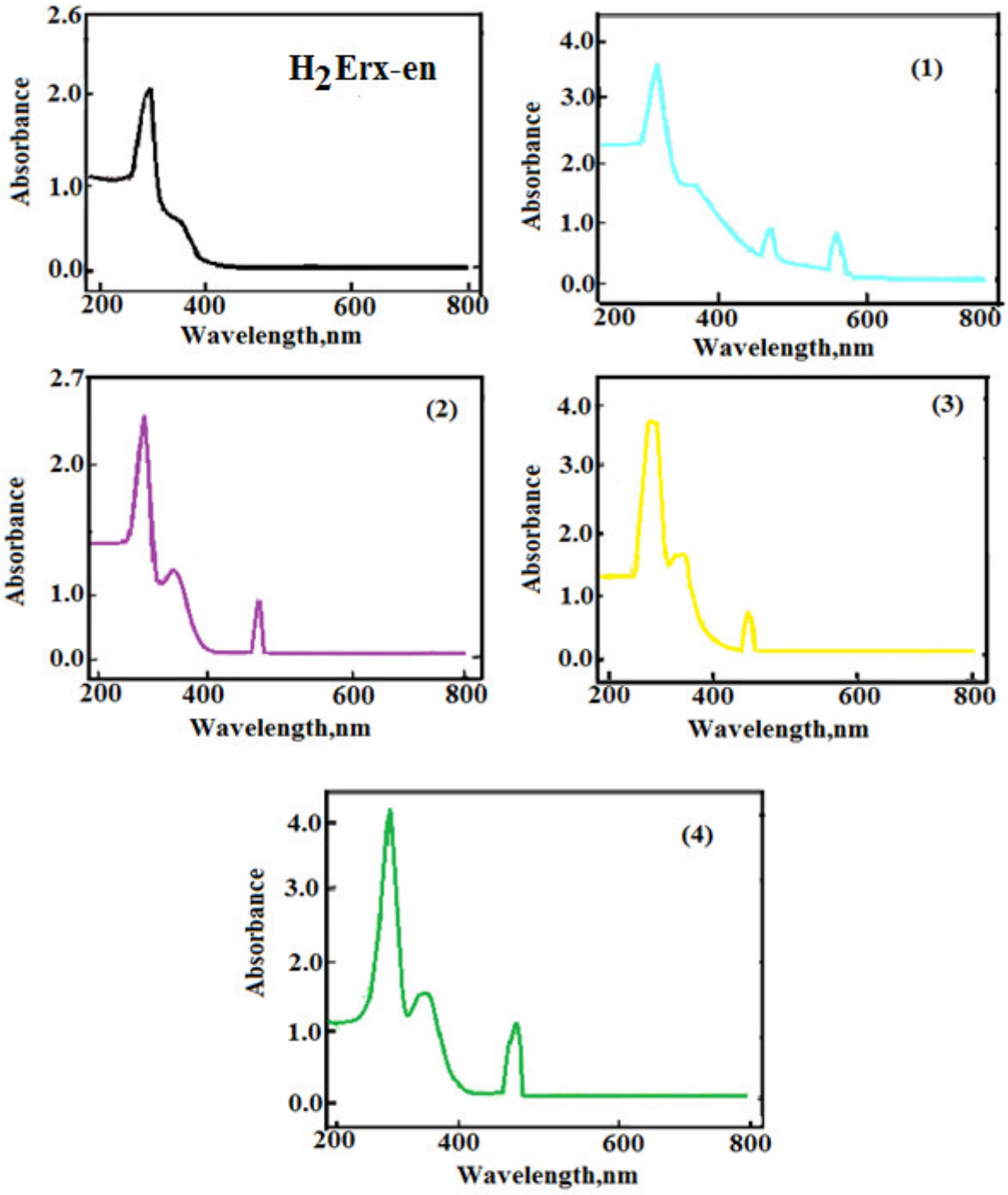



**Figure S2.** Electronic absorption spectra for **$H_2$Erx-en** and its metal complexes

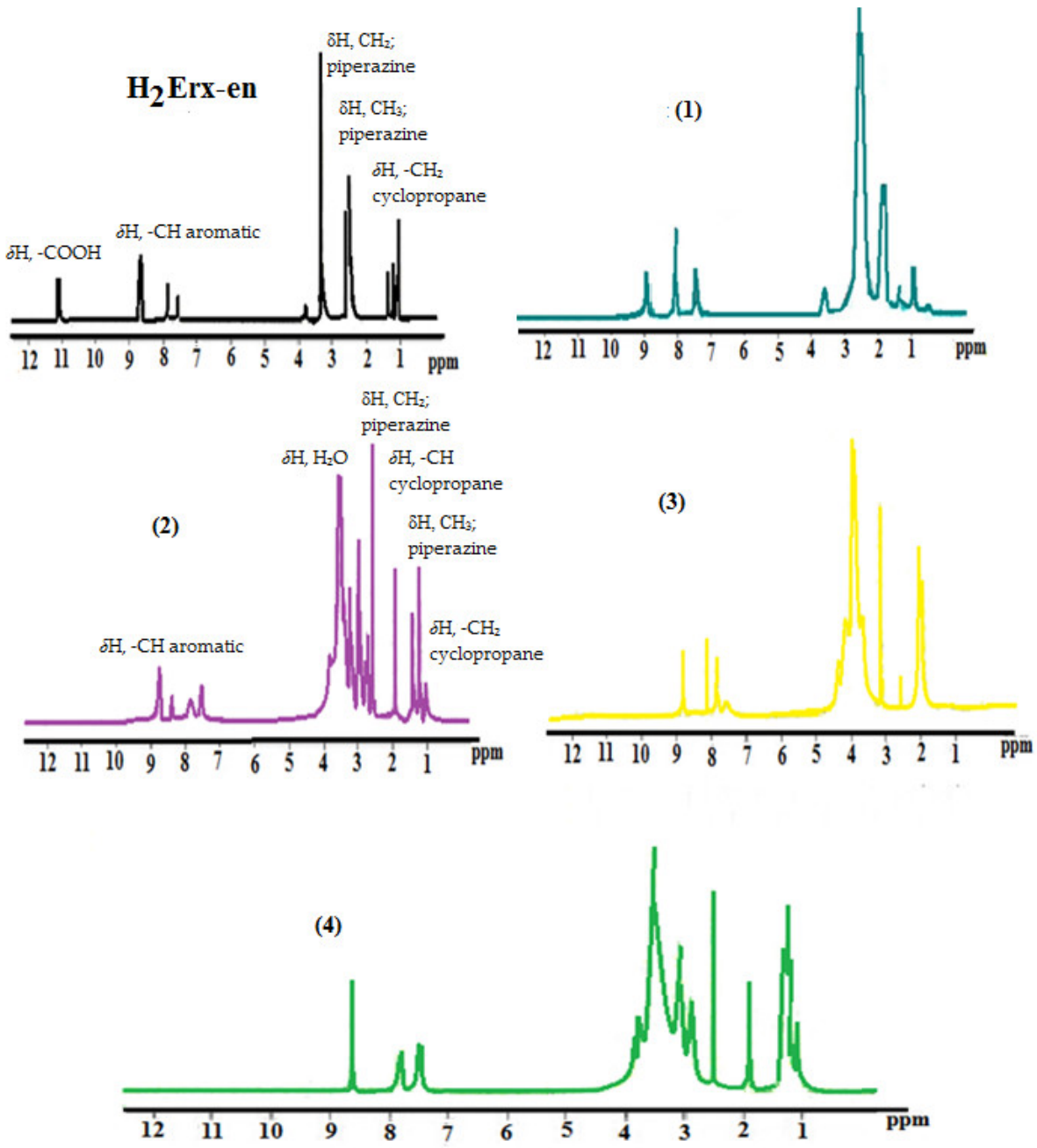



**Figure S3**. $^{1}$H NMR spectra for **H$_2$Erx-en** and its metal complexes

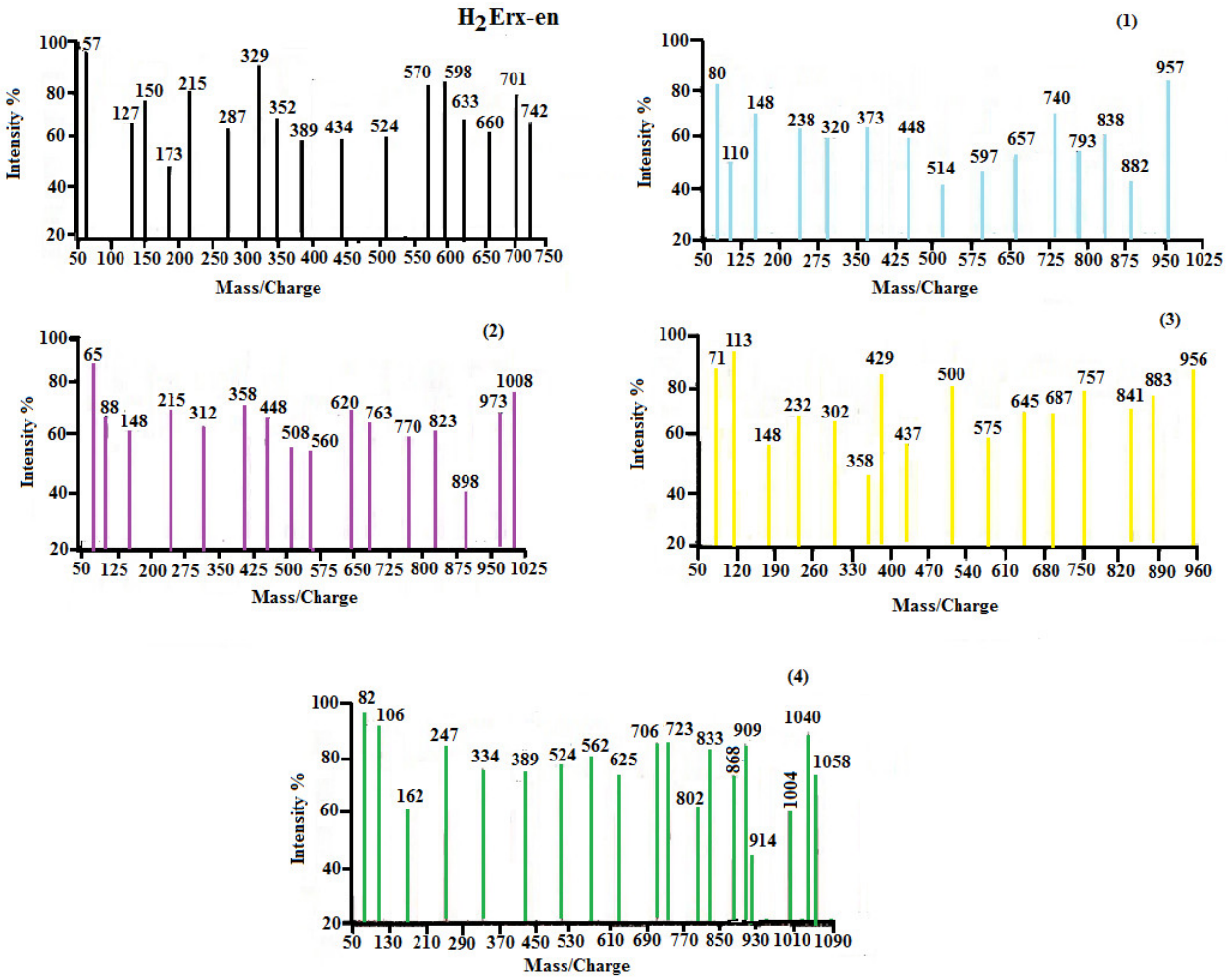



**Figure S4.** Mass spectra diagrams for **$H_2$Erx-en** and its metal complexes

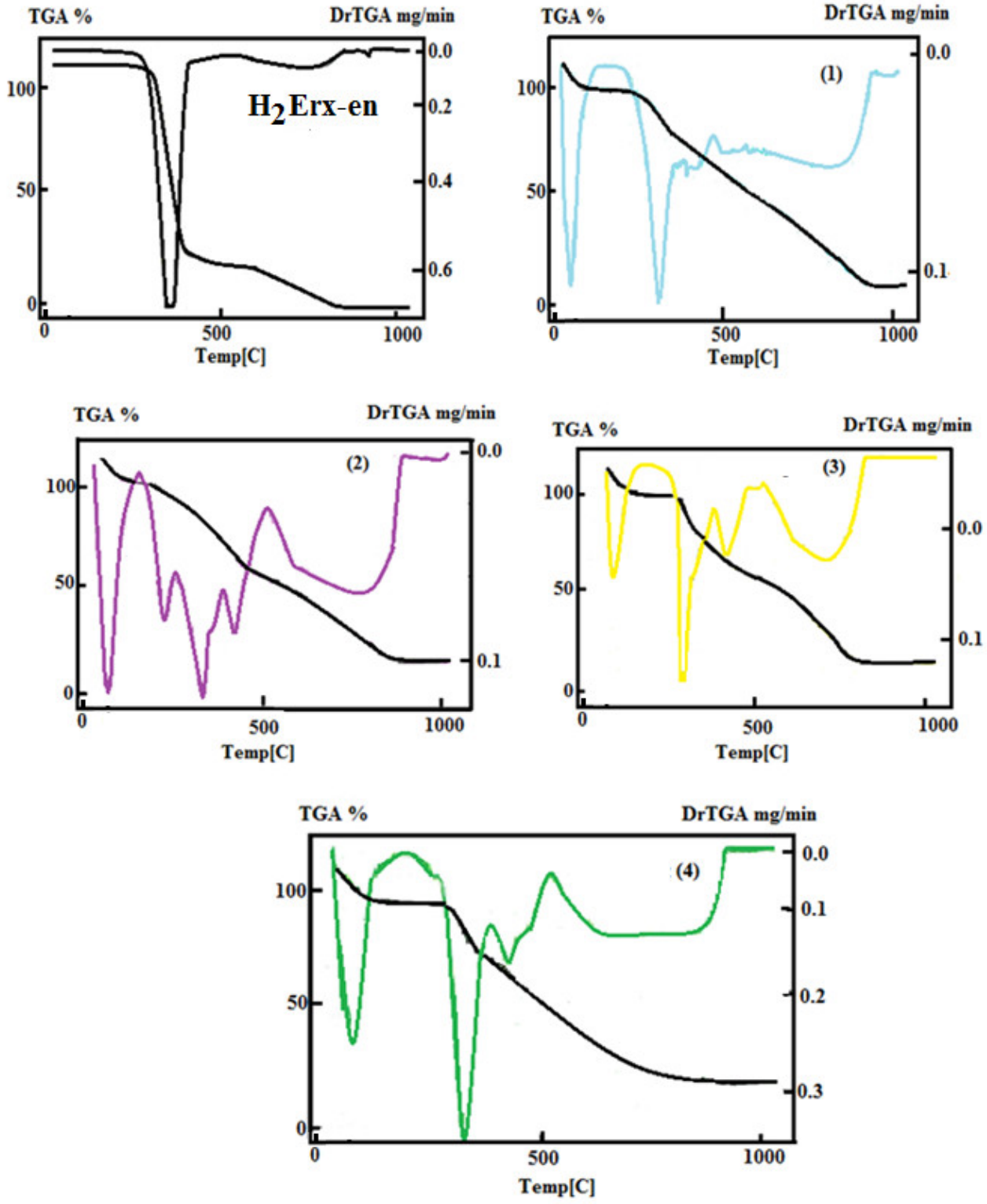
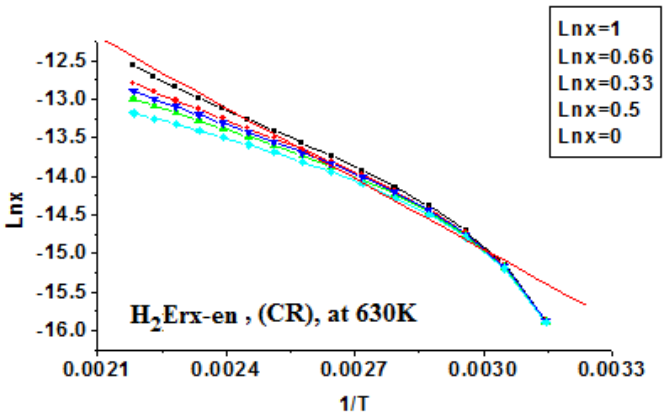



**Figure S5.** TG and DTG diagrams for **$H_2$Erx-en** and its metal complexes.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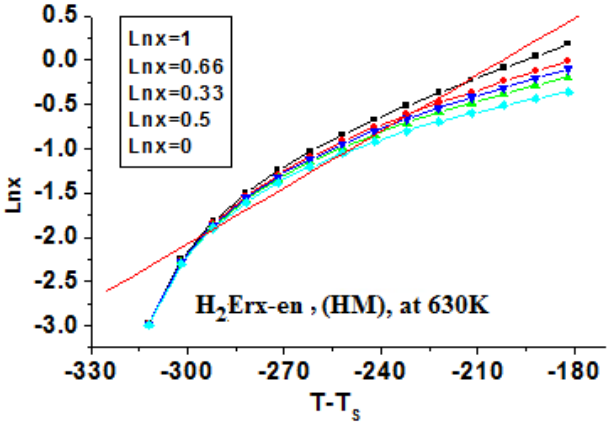
Lnx=0.33
Lnx=0.5
Lnx=0
Lnx
1/T
H2Erx-en , (CR), at 630K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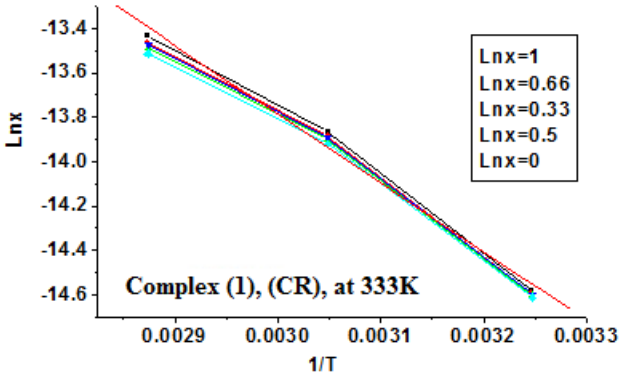
Lnx
T-Ts
H2Erx-en , (HM), at 630K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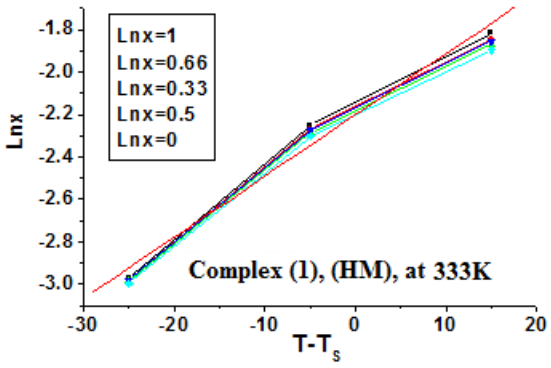
1/T
Complex (1), (CR), at 333K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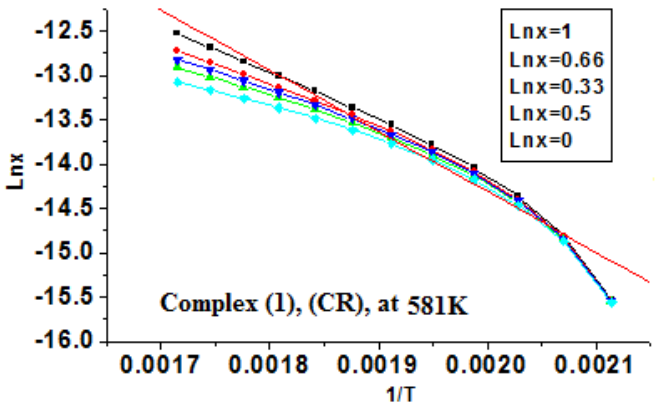
Lnx=0.5
Lnx=0
Lnx
T-Ts
Complex (1), (HM), at 333K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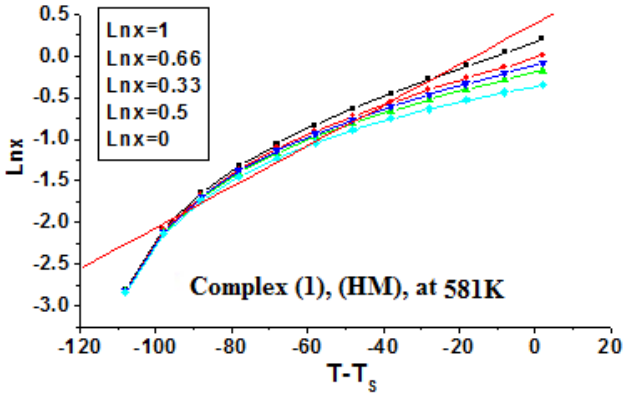
1/T
Complex (1), (CR), at 581K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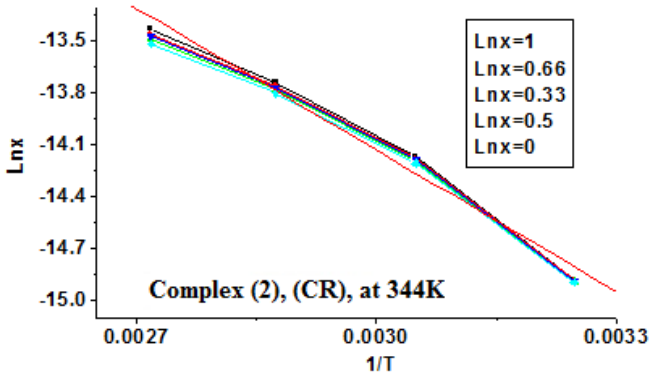
Lnx=0
Lnx
T-Ts
Complex (1), (HM), at 581K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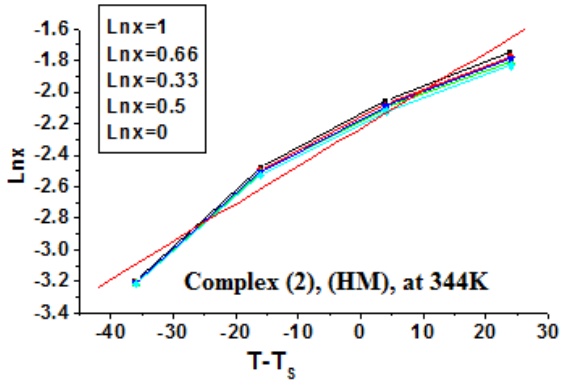
Complex (2), (CR), at 344K
Lnx
1/T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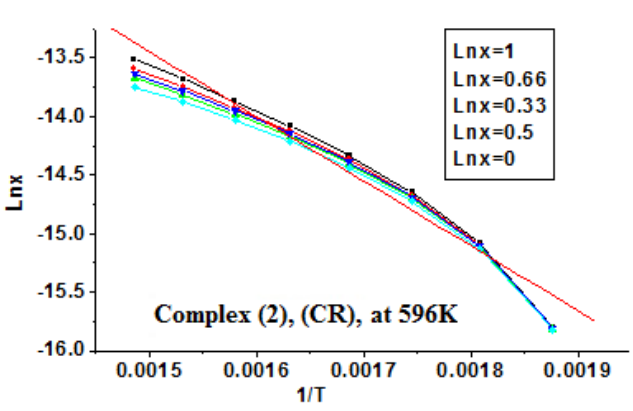
Complex (2), (HM), at 344K
Lnx
T-T$_S$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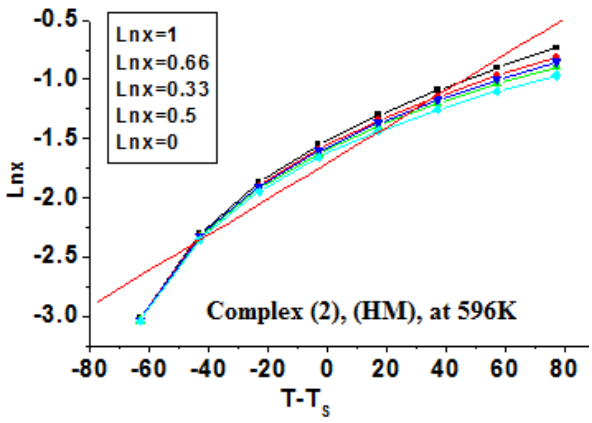
Complex (2), (CR), at 596K
Lnx
1/T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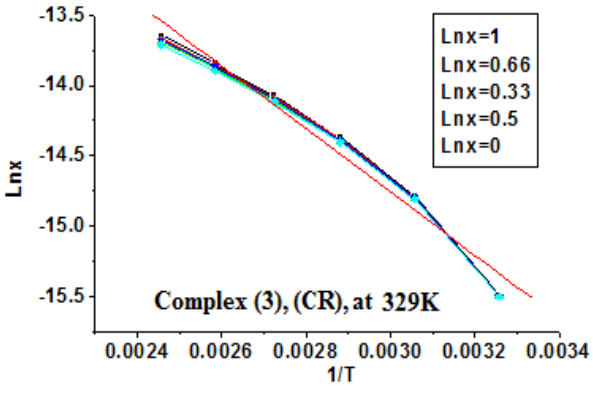
Lnx=0
Complex (2), (HM), at 596K
Lnx
T-T$_S$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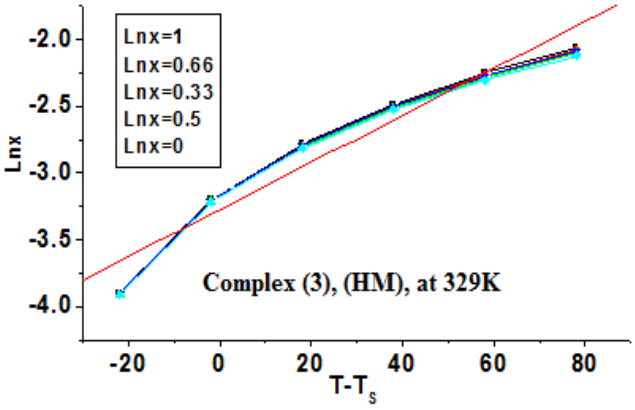
Lnx=0
Complex (3), (CR), at 329K
Lnx
1/T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Lnx=0.66
Lnx=0.33
Lnx=0.5
Lnx=0
Complex (3), (HM), at 329K
Lnx
T-T$_S$

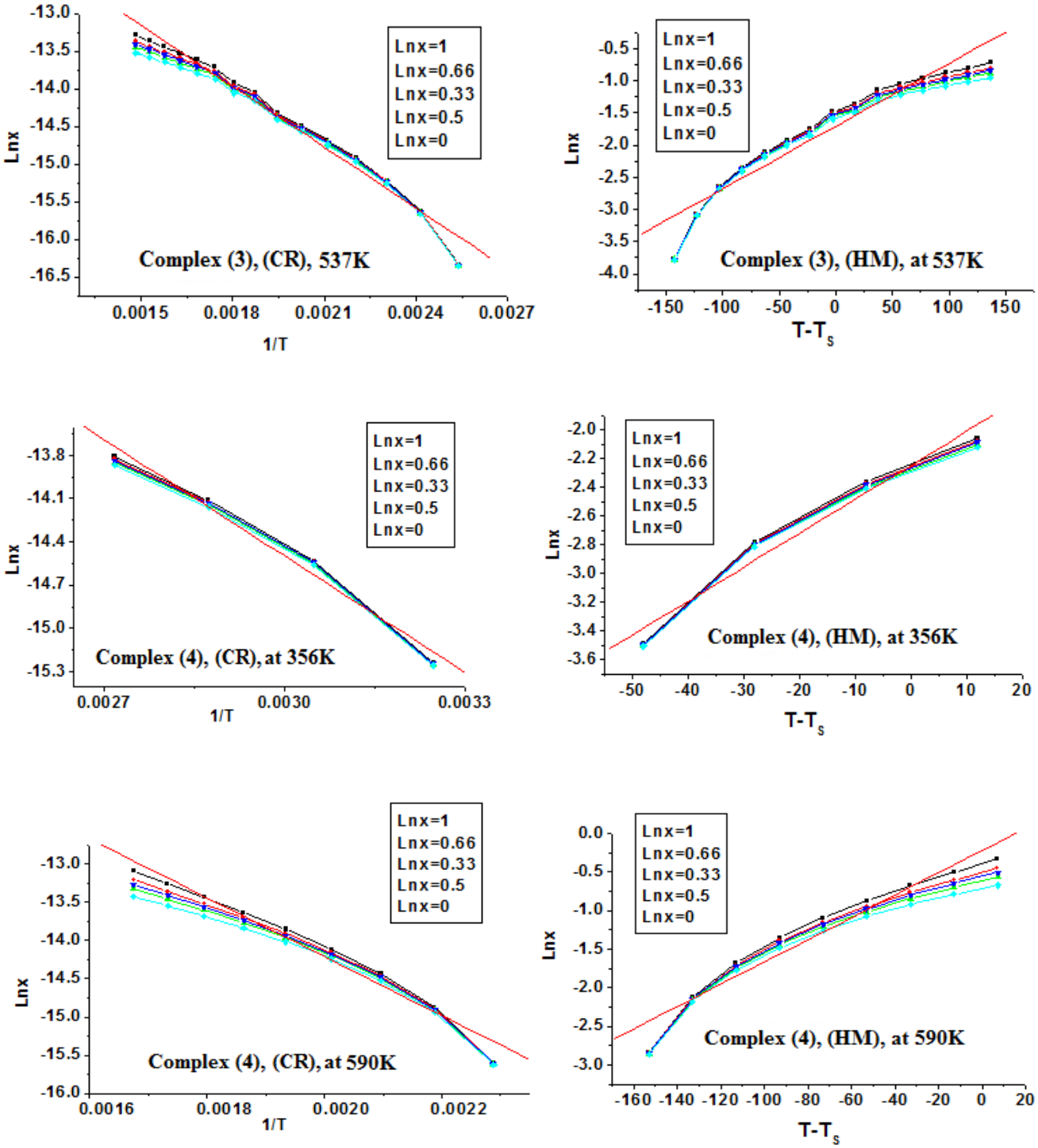



**Figure S6.** The diagrams of kinetic parameters of **$H_2$Erx-en** and its metal complexes using Coats-Redfern(CR) and Horowitz-Metzger (HM) equations

**Table S1**. The inhibition diameter zone (mm) values for **$H_2$Erx-en** and its metal complexes

| Tested compounds | Microbial species | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Bacteria | | | | | | | | | | | | Fungi | |
| | *E. coli* | MIC | AI | *Salm. typhi* | MIC | AI | *S. aureus* | MIC | AI | *B. cereus* | MIC | AI | *C. albicans* | *P. vulpinum* |
| **$H_2$Erx-en** | 0 | 0 | 0 | $30^{+3}$ ±1 | 0.75 ±0.01 | 184.0 | $28.6^{+3}$ ±0.8 | 1.00 ±0.03 | 210.2 | 0 | 0 | 0 | 0 | 0 |
| **(1)** | 0 | 0 | 0 | 0 | 0 | | $31.6^{+3}$ ±2 | 0.75 ±0.03 | 232.3 | $3.3^{+2}$ ±0.1 | 0.50 ±0.007 | 20.2 | 0 | 0 |
| **(2)** | 0 | 0 | 0 | 0 | 0 | 0 | $33.6^{+3}$ ±0.8 | 0.75 ±0.006 | 247.0 | 0 | 0 | 0 | 0 | 0 |
| **(3)** | 0 | 0 | 0 | 0 | 0 | 0 | $27.6^{+3}$ ±0.8 | 0.75 ±0.01 | 202.9 | 0 | 0 | 0 | 0 | 0 |
| **(4)** | 0 | 0 | 0 | $27.6^{+3}$ ±1 | 0.50 ±0.005 | 169.3 | 0 | 0 | 0 | $2.3^{+3}$ ±0.1 | 0.75 ±0.03 | 0 | 0 | 0 |
| **Ciprofloxacin** | $20^{+3}$ ±1 | - | | 0 | 0 | | $13.6^{+3}$ ±0.8 | | | | | | 0 | 0 |
| **Amikacin** | $14^{+3}$ ±1 | - | | $16.3^{+3}$ ±0.3 | - | | $8.6^{+3}$ ±0.8 | - | | $5.3^{+3}$ ±0.3 | | | 0 | 0 |
| **Cefuroxime** | 0 | - | | $14^{+3}$ ±1 | - | | $18.3^{+3}$ ±0.8 | - | | 0 | | | 0 | 0 |
| **Cefpodexime** | 0 | - | | $7^{+3}$ ±0.5 | - | | $19^{+3}$ ±1 | - | | 0 | | | 0 | 0 |
| **Ceftazidime** | 0 | - | | $15.3^{+3}$ ±2 | - | | $3^{+3}$ ±0.5 | - | | 0 | | | 0 | 0 |
| **Ethylene diamine** | 0 | - | | $15^{+3}$ ±0.5 | - | | 0 | - | 0 | 0 | | | 0 | 0 |
| **DMF** | 0 | - | | 0 | - | | 0 | - | 0 | 0 | - | | 0 | 0 |

Statistical significance PNS P not significant, P <0.05; P+1 P significant, P>0.05; P+2 P highly significant, P>0.01; P+3 P very highly significant, P>0.001; student'st-test (Paired).

**Table S2.** Equilibrium geometric parameters bond lengths (Å), bond angles (˚),dihedral angles (˚), total energy (k cal/mol) and dipole moment of **$H_2$Erx-en** using DFT calculations.

| Bond length (Å) | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2-C3 | 1.343 | N4-C5 | 1.345 | C7-O8 | 1.209 | C13-C14 | 1.346 |
| N1-C2 | 1.351 | C5-C6 | 1.346 | C7-O9 | 1.337 | C11-C13 | 1.364 |
| C3-N4 | 1.345 | C6-C7 | 1.364 | N1-C14 | 1.348 | C11-O10 | 1.335 |
| | | | | | | C11-O12 | 1.210 |

| Bond angle (˚) | | | | | |
|---|---|---|---|---|---|
| N1C2C3 | 128.19 | C6C7O8 | 123.05 | C14C13C11 | 122.17 |
| C2C3N4 | 120.99 | C6C7O9 | 121.75 | C13C11O10 | 123.89 |
| C3N4C5 | 121.83 | O8C7O9 | 115.19 | C13C11O12 | 120.32 |
| N4C5C6 | 121.26 | C2N1C14 | 116.47 | O12C11O10 | 115.69 |
| C5C6C7 | 123.58 | N1C14C13 | 120.39 | | |

| Dihedral angles (˚) of ($H_2$Erx-en) | | | |
|---|---|---|---|
| C5C6C7O9 | -179.29 | O8C7C6C5 | 1.29 |
| C7C6C5N4 | 2.44 | C6C5N4C3 | -87.03 |
| C5N4C3C2 | -177.92 | N4C3C2N1 | -0.344 |
| C3C2N1C14 | 3.87 | C2N1C14C13 | -94.46 |
| N1C14C13C11 | -4.51 | C14C13C11O10 | 0.458 |
| C14C13C11O12 | -178.89 | | |

| Dihedral angles (˚) of enrofloxacin molecule (Enro) | | | |
|---|---|---|---|
| C8C12C16O17 | -4.02 | C6N9C13C14 | 126.91 |
| C21N20C1C4 | -81.72 | C6N9C13C15 | 61.16 |
| C4C1N20C25 | 90.62 | C10C12C16O18 | 0.25 |
| C1N20C25C24 | 136.88 | C10C12C16O17 | -179.55 |
| N20C25C24N23 | 49.68 | O11C8C12C16 | 7.46 |
| C25C24N23C26 | 87.48 | C27C26N23C24 | -81.48 |
| Total energy/ k cal/mol | | -311211.5866330 | |
| Total dipole moment/D | | 10.56 | |

**Table S3.** Equilibrium geometric parameters bond lengths (Å), bond angles (˚),dihedral angles (˚), Total energy (k cal/mol) and Dipole moment of the studied complexes using DFT calculations.

| Bond lengths/ Å | **(1)** | **(2)** | **(3)** | **(4)** |
|---|---|---|---|---|
| M-N1 | 1.982 | 2.595 | 2.315 | 2.751 |
| M-O10 | 1.930 | 2.393 | 2.193 | 2.439 |
| M-N4 | 1.973 | 2.607 | 2.318 | 2.753 |
| M-O9 | 1.935 | 2.406 | 2.207 | 2.499 |
| M-O15 | 1.999 | 2.357 | 2.139 | 2.448 |
| M-O16 | 2.111 | 2.361 | 2.097 | 2.455 |
| N1-C2 | 1.265 | 1.269 | 1.271 | 1.269 |
| C2-C3 | 1.346 | 1.343 | 1.344 | 1.345 |
| C3-N4 | 1.269 | 1.268 | 1.270 | 1.269 |
| N1-C14 | 1.276 | 1.280 | 1.279 | 1.281 |
| C13-C14 | 1.357 | 1.358 | 1.356 | 1.359 |
| C11-C13 | 1.362 | 1.363 | 1.361 | 1.364 |
| C11-O10 | 1.346 | 1.342 | 1.343 | 1.345 |
| C11-O12 | 1.209 | 1.211 | 1.210 | 1.212 |
| N4-C5 | 1.275 | 1.281 | 1.279 | 1.280 |
| C5-C6 | 1.355 | 1.357 | 1.356 | 1.359 |
| C6-O7 | 1.363 | 1.361 | 1.362 | 1.360 |
| C7-O9 | 1.342 | 1.341 | 1.343 | 1.342 |
| C7-O8 | 1.211 | 1.210 | 1.212 | 1.211 |
| N1-M-N4 | 79.71 | 70.37 | 74.87 | 69.54 |
| N1-M-O9 | 166.07 | 129.83 | 130.34 | 132.79 |
| N1-M-O10 | 85.54 | 75.96 | 81.83 | 73.03 |
| N1-M-O15 | 100.54 | 150.98 | 83.21 | 130.21 |
| N1-M-O16 | 105.69 | 78.94 | 145.39 | 92.21 |
| N4-M-O9 | 96.34 | 75.37 | 79.53 | 74.76 |
| N4-M-O10 | 113.26 | 130.03 | 139.28 | 127.97 |
| N4-M-O15 | 157.17 | 134.35 | 89.78 | 151.68 |
| N4-M-O16 | 81.26 | 119.24 | 133.31 | 82.59 |
| O9-M-O10 | 83.72 | 101.02 | 91.32 | 108.73 |
| O9-M-O15 | 88.32 | 77.57 | 138.75 | 95.18 |
| O9-M-O16 | 86.79 | 151.06 | 80.73 | 112.81 |
| O10-M-O15 | 89.43 | 90.77 | 120.35 | 80.23 |
| O10-M-O16 | 163.41 | 88.09 | 82.79 | 133.92 |
| O15-M-O16 | 76.69 | 74.88 | 78.20 | 77.09 |
| Total energy, k cal/mol | -347128.827 | -333986.825 | -333922.301 | -335273.485 |
| Dipole moment, D | 12.852 | 14.597 | 22.480 | 13.286 |

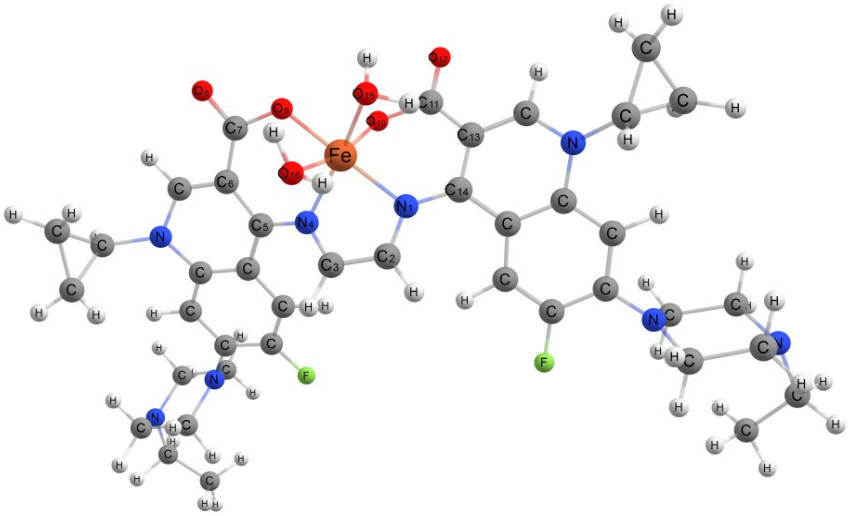
**Table S4.** Calculated charges on donating sites and energy values (HOMO, LUMO, Energy gap ΔE/eV, hardness (η), global softness (S), electro negativity (χ), absolute softness (σ), chemical potential (Pi), global electrophilicity (ω) and additional electronic charge ($\Delta N_{max}$) of $H_2$Erx-en and its metal complexes using DFT calculation

| Parameters | **$H_2$Erx-en** | **(1)** | **(2)** | **(3)** | **(4)** |
|---|---|---|---|---|---|
| M | - | 0.089 | 0.448 | 0.307 | 0.406 |
| N1 | -0.285 | -0.094 | -0.172 | -0.143 | -0.173 |
| N4 | -0.087 | -0.116 | -0.175 | -0.154 | -0.187 |
| O9 | -0.362 | -0.450 | -0.433 | -0.373 | -0.422 |
| O10 | -0.391 | -0.445 | -0.417 | -0.379 | -0.426 |
| O15 | - | -0.326 | -0.299 | -0.531 | -0.335 |
| O16 | - | -0.332 | -0.324 | -0.305 | -0.313 |
| C2 | 0.165 | 0.086 | 0.017 | 0.018 | 0.007 |
| C3 | -0.043 | 0.066 | 0.021 | 0.037 | 0.039 |
| C5 | -0.120 | 0.228 | 0.255 | 0.248 | 0.267 |
| C6 | -0.057 | -0.153 | -0.186 | -0.172 | -0.183 |
| C7 | 0.482 | 0.472 | 0.489 | 0.493 | 0.492 |
| O8 | -0.454 | -0.450 | -0.464 | -0.461 | -0.443 |
| C14 | 0.302 | 0.249 | 0.253 | 0.239 | 0.250 |
| C13 | -0.146 | -0.136 | -0.183 | -0.167 | -0.195 |
| C11 | 0.517 | 0.483 | 0.491 | 0.498 | 0.481 |
| O12 | -0.429 | -0.451 | -0.456 | -0.456 | -0.446 |
| HOMO,H | -0.308 | -0.309 | -0.310 | -0.311 | -0.315 |
| LUMO,L | -0.245 | -0.297 | -0.289 | -0.302 | -0.310 |
| I = -H | 0.308 | 0.309 | 0.310 | 0.311 | 0.315 |
| A = -L | 0.245 | 0.297 | 0.289 | 0.302 | 0.310 |
| ΔE = L-H | 0.063 | 0.012 | 0.021 | 0.009 | 0.005 |
| η = (I-A)/2 | 0.0315 | 0.006 | 0.0105 | 0.0045 | 0.0025 |
| χ = -(H-L/2) | 0.2765 | 0.303 | 0.2995 | 0.3065 | 0.3125 |
| σ = 1/ η | 31.476 | 166.667 | 95.238 | 222.22 | 400.00 |
| S = 1/2 η | 15.873 | 83.333 | 47.619 | 111.11 | 200.00 |
| Pi = - χ | -0.2765 | -0.303 | -0.2995 | -0.3065 | -0.3125 |
| $\omega = (Pi)^2/2\ \eta$ | 1.2135 | 7.651 | 4.271 | 10.438 | 19.531 |
| $\Delta N_{max} = \chi/\ \eta$ | 8.778 | 50.5 | 28.524 | 68.111 | 125.00 |

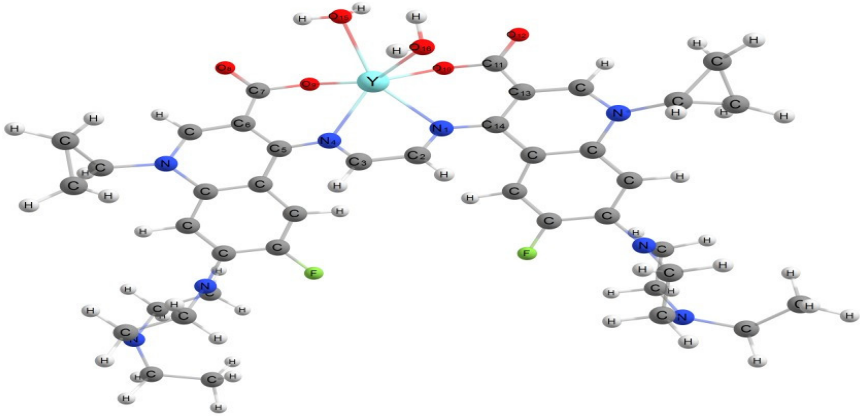
( I ) is ionization energy, ( A ) is an electron affinity

**Table S5.** Composition of the frontier molecular orbital for the obtained stable complexes using DFT/B3LYP/Cep-31G.

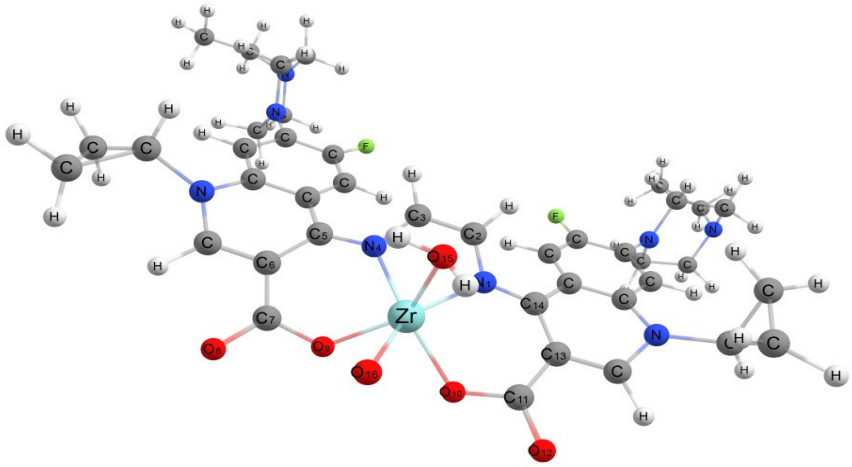
| | (1) | | | (2) | |
|---|---|---|---|---|---|
| | H | L | | H | L |
| **Fe(111)** | 0.3% | 0.0% | **Y(III)** | 0.0% | 0.0% |
| **Enerofloxacin** | 99.7% | 100% | **Enerofloxacin** | 100% | 72.4% |
| **ethylenediamine** | 0.0% | 0.0% | **ethylenediamine** | 0.0% | 27.6% |
| **O15** | 0.0% | 0.0% | **O15** | 0.0% | 0.0% |
| **O16** | 0.0% | 0.0% | **O16** | 0.0% | 0.0% |
| | **(3)** | | | **(4)** | |
| | H | L | | H | L |
| **Zr(IV)** | 0.0% | 0.0% | **La(III)** | 0.0% | 66.8% |
| **Enerofloxacin** | 100% | 100% | **Enerofloxacin** | 100% | 10.4% |
| **ethylenediamine** | 0.0% | 0.0% | **ethylenediamine** | 0.0% | 22.8% |
| **O15** | 0.0% | 0.0% | **O15** | 0.0% | 0.0% |
| **O16** | 0.0% | 0.0% | **O16** | 0.0% | 0.0% |



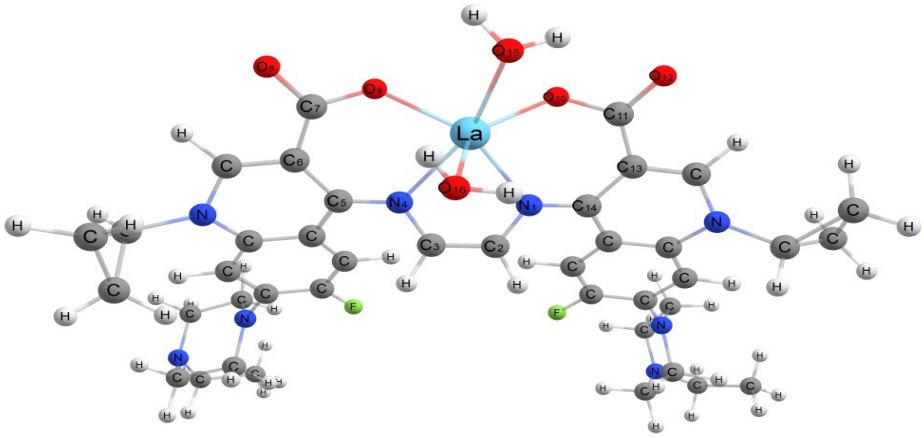

**Scheme S1.** Optimized geometrical structure of complex **(1)** using DFT calculations.



**Scheme S2.** Optimized geometrical structure of complex **(2)** using DFT calculations.




**Scheme S3.** Optimized geometrical structure of complex **(3)** using DFT calculations.




**Scheme S4.** Optimized geometrical structure of complex **(4)** using DFT calculations.