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# SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL ACTIVITIES OF 1, 2 NAPHTHOQUINONE-1-OXIME LIGAND AND ITS METAL CHELATES OF Hg (II), Pb (II), Ag (I), Zn (II) AND Cd (II)

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## ABSTRACT

Five metal chelates of the type M $[NQO]_2$ where M = Hg, Cd, Ag, Zn, Pb, NQO = 1, 2 napthoquinone-1-oxime and Ag(NQO) have been synthesized. All chelates have been characterized by modern methods such as elemental analysis, FTIR, Electronic spectra. $^1H$ & $^{13}C$ NMR, Thermogravimetry and Differential scanning calorimetry and electron microscopy with EDAX analysis. All chelates are found to be coloured and mercury, lead, zinc and cadmium chelates are octahedral while silver chelate has been assigned square planer. These chelates are thermally stable up to 700°C and all are crystalline in nature. Their particle sizes are in the range of 30-50 nm. The ligand and the metal chelates have been screened for antimicrobial activity on gram positive and gram negative bacteria and fungi.

**Key words**: 1-Nitroso-2, naphthol, 1-2 Naphthoquinone-1, Oxime, IR, NMR, SEM, Antimicrobial activity, Electronic spectra.

## INTRODUCTION

Metal chelates of 1-2-naphthoquinone-1 oxime containing Cu, Mn, Fe and Zn have been prepared by Lamb et al.[1] These complexes can be used for the prevention and control of fungal infestations of agricultural, organic and related articles by using composition in

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which these metal chelates are part of the constituent. Wirth et al.[2] reported Rhodium (III) and Iridium (III) complexes of 1, 2-naphthoquinone-1-oxime and characterized as potential anticancer agents, in respect to their neurotoxicity, to induce programmed cell death (apoptosis) and their impact on double strand DNA (ds DNA).

Dhapte[3] reported that La (III), Ce (III), Nd (III) and Sm (III) metal chelates have shown antimicrobial activity. Substances containing the nitroso-hydroxy moiety are associated with antimicrobial activity[4]. Lanthanide metal chelates of NQO have been used as biological probes[5]. The present paper describes the synthesis, characterization such as XRD, IR, Electronic spectra, NMR, SEM, TG, DSC and antimicrobial activity of metal chelates of 1,2-naphthoquinone-1-oxime (NQO) with metals like Hg (II), Pb (II), Cd (II) Ag (I) and Zn (II).

## EXPERIMENTAL

### Materials and methods

The ligand 1, 2-naphthoquinone-1-oxime or 1-nitroso-2-naphthol is used as it is supplied by AR grade Thomas Baker chemicals. A stock solution of Pb (II), Zn (II), Cd (I), Hg (II) and Ag (I) is prepared by using AR grade chemicals. Deionised water is used during synthesis.

### Preparation of metal chelates

The chelates were prepared by mixing metal salt solution and ligand in 1 : 1 proportion for silver chelate and 1 : 2 for other metals. The mixture was constantly stirred for one hour on magnetic stirrer. The pH of the mixture was maintained, in between 5.0 – 6.0 by adding ammonia solution to it. Warm the mixture on water bath for about 15 minutes. On cooling it was filtered and found to be coloured.

### Instrumental Analysis

Elemental analysis is carried out with a Perkin Elmer 2400 series for C, H, O and N. The IR spectra are recorded on a Shimadzu FTIR 8400 S model in a KBr matrix. Electronic spectra are recorded on Perkin Elmer UV–visible spectrometer, Lambda-25 model. TGA curves are recorded on Perkin Elmer Pyris. TGA apparatus using $10^{o}C$/min in air and DSC on DSC 800 model. The proton and $^{13}C$ NMR spectra recorded in DMSO dueterated on Varion. 400 MR powder X ray diffraction patterns are obtained by using Rigaku Miniflex (II). LC – MS scans is carried out on Shimadzu – LCMS 2010 employing electron impact source. Scanning electron microscopy was carried out on Vega 2SB model and EDAX on OXFORD INCA PENTA with TECAN VEGA 2SB.

### Antimicrobial activity testing

Test organisms: The antimicrobial activity of ligands, metal salts and synthesized metal chelates is tasted against bacteria [*Escherichia coli* (NCIM 2065), *Bacillus subtilis* (NCIM 2063), *Staphylococcus aureus* (NCIM 2079), *Proteus Vulgaris* (NCIM 2813), *P. aeruginosa* (NCIM 2200), *Aspergillius niger* (NCIM 1196) and *Candida albicans* (NCIM 3471)] strains collected from NCL, Pune India.

### Maintenance of culture

The cultures of bacteria and fungi were maintained on Nutrient agent (Himedia Laboratories Pvt. Ltd. Ref. M 002-500G 99% Purity), Mueller-Hinton Agar (Himedia Laboratories Pvt. Ltd Ref. M 173 – 500G, 99% Purity) and subcultured accordingly and preserved at $4^o$ C. for 24 hours in incubator.

### Plating

The 100 μL cell suspension ($10^8$ cell/mL of bacteria & yeasts C. albicans and 100 μL of spore suspension of mold (A. niger) were spread on then. Agar (for bacteria) and Mueller-Hinton Agar for fungi. Then wells were bored in the media. In the wells DMSO (solvent), ligand, metal salts and metal chelate solutions were poured for each organism, and then incubated at $37^oC$ for 48 hrs. for bacteria and $30^oC$ for 5 days for fungi. The zone diameter of inhibition were measured in mm and recorded.

## RESULTS AND DISCUSSION

### Thermal analysis

The TG, DTG and DSC data is given in Table 1. The ligand 1-nitroso-2-naphthol or 1,2 naphthoquinone-1 oxime (NQO) is heated with $10^oC$/min in air up to $380^oC$ and DSC was carried out by heating $10^oC$/min from $30^oC$ to $200^oC$ in $N_2$. The TG shows first weight loss corresponds to the loss of (N-OH) which is in good agreement in the range of 101-$160^oC$ (17.91% and found as 18.2%). The second step is continuous weight loss up to 48.2% up to $380^oC$ which is probably due to loss of $C_4H_4NO$ moiety. It indicates that the ligand has high chemical stability. DTG are also given in Table 1. DSC data shows that one exotherm in the range 104.30 to $115^oC$ and maximum peak at $107.40^oC$ and ΔH found to be 125.39 J/g. It can be assigned to loss of N-OH moiety.

TG data of metal chelates of Pb, Zn and Hg shows more or equal results for the first step decomposes about 100-160°C and weight loss up to 18 ± 2% and DTG temperatures are in the range of 148-154°C. Ag (NQO) shows similar results. In the case of Cd $(NQO)_2$ the loss in weight is up to 40.2% in the temperature range 100-180°C and later the decompositions process continues.

DSC data of metal chelates shows that the chelates containing Pb, Zn, Hg and Cd exhibits an exotherm in the range 104 to 116°C and peak temperature about at 107 ± 2°C. There is a variation of the absorption of heat as it can be seen from the Table 1. In the case of Ag (NQO) it shows an endotherm in the range 156.29°C to 190°C with peak temperature at 162.15°C. The enthalpy of the process is recorded as -334.871 J/g.

**Table 1: Thermo analytical data of ligand and its chelates**

| S. No. | Compound | Temp Range °C | % loss | DTG PEAK (°C) |
|---|---|---|---|---|
| 1 | NQO | 100-160 | 18.0 | 154 |
| 2 | Pb $(NQO)_2$ | 100-160 | 18.0 | 148 |
| 3 | Zn $(NQO)_2$ | 95-160 | 15.0 | 150 |
| 4 | Ag(NQO) | 140-150 | 14.0 | 150 |
| 5 | Hg $(NQO)_2$ | 101-155 | 18.0 | 148 |
| 6 | Cd $(NQO)_2$ | 100-180 | 86.2 | -- |
| | | 180-350 | 15.0 | -- |

**Table 2: Calorimetric data decomposition of ligand and its chelates**

| S. No. | Compound | DSC EXO | | | ΔH J/g |
|---|---|---|---|---|---|
| | | I (°C) | II (°C) | III (°C) | |
| 1 | NQO | 104.58 | 107.40 | 115.0 | 125.39 |
| 2 | Pb $(NQO)_2$ | 107.76 | 109.30 | 116.0 | 72.44 |
| 3 | Zn $(NQO)_2$ | 106.88 | 108.45 | 114.0 | 82.00 |
| 4 | Ag(NQO) | 156.29 | 162.50 | 170.0 | -334.87 |
| 5 | Hg $(NQO)_2$ | 106.99 | 108.13 | 116.0 | 101.82 |
| 6 | Cd $(NQO)_2$ | 106.19 | 108.73 | 117.0 | 48.80 |

I = Inception temp., II = Peak temp. and III = End temp.

## Kinetics

To calculate kinetic parameters of 1, 2-naphthoquinone-1, oxime a separated TG/DTG was run on Shimadzu STA in the ranges 0.0°C to 800°C in air. The first step decomposition starts at 112.64°C and ends at 225.90°C. The observed weight loss was – 14.669%. The TG data was used to calculate kinetic parameters by using developed software[9]. The kinetic parameters for F-5 model calculated using Coates-Redfern equation which random nucleation (Mampel unimolecular law). The results re given in Table 3.

**Table 3: Kinetic parameters for decomposition of NQO in air**

| S. No. | Parameter | Step I 112.6 to 225.5°C | Step II 247.1 to 486.93°C |
|---|---|---|---|
| 1 | n-Order of reaction | 1 | 1 |
| 2 | E-Energy of activation | 35.05 KJ/mol | 55.53 KJ/mol |
| 3 | R-regression coefficient | 0.8672 | 0.99331 |
| 4 | Log A-Frequency factor | 1.8672 | 2.3814 |
| 5 | S-Entropy of activation | -219.2278 J/mol/K | -228.6446 J/mol/K |
| 6 | G-Free energy of activation | 175.0174 KJ/mol | 194.0612 KJ/mol |
| 7 | H-Enthalpy of activation | 73.7247 KJ/mol | 55.4390 KJ/mol |

A solid state reaction was proposed for the decomposition of NQO, since it decomposes without melting[6-8].

## X-ray diffraction

X-ray diffraction data was obtained using Rigaku X-ray diffractometer ($CuK_{\alpha}$ radiation) Miniflex 2 and the data such as d values in $A^0$ and ratio $I/I_0$values are given in Table 4 for 1, 2 naphthoquinone-1.

**Tabe 4: XRD data of 1, 2 naphthoquinone-1, oxime or 1-nitroso-2 naphthol (NQO)**

| S. No. | d (Å) | $I/I_O$ |
|---|---|---|
| 1 | 7.9360 | 50 |
| 2 | 6.0456 | 11 |

Cont…

| **Sr. No.** | **d (Å)** | **$I/I_O$** |
|---|---|---|
| **3** | 5.5142 | 45 |
| **4** | 5.0350 | 32 |
| **5** | 4.7162 | 15 |
| **6** | 4.5577 | 52 |
| **7** | 4.2997 | 10 |
| **8** | 4.0153 | 39 |
| **9** | 3.8803 | 34 |
| **10** | 3.7355 | 14 |
| **11** | 3.5786 | 31 |
| **12** | 3.4165 | 100 |
| **13** | 3.1422 | 62 |
| **14** | 3.0599 | 15 |
| **15** | 2.8769 | 10 |
| **16** | 2.8238 | 13 |
| **17** | 2.7011 | 15 |

Fig. 1 shows XRD patterns of oxime metal chelates containing Zn (II), Hg (II), Cd (II) and Ag (I). It is observed that all these chelates are crystallite in nature. The data was processed by using McMaille[10] and found that 1-nitroso-2-naphthol is monoclinic which is recorded at 300 K. The reported data is comparable which was recorded at 200 K[3]. The crystal data shows a = 5.4567, b = 9.2861 and c = 15.8238 Å, β = 103.884, volume 778.351 $(Å)^3$, the density was considered as 1.608161g/$cm^3$ and Z = 4. It is reported that the torsion angle between O-H group and naphthalene ring becomes near $0^o$.[11] In strong hydrogen bonds the distance between the oxygen atoms 0 - - 0 is 2.40 – 2.58 Å. According to this criterion the hydrogen bonds in this compound belongs to strong ones. The metal chelates of Zn $(NQO)_2$, shows data as per computer code referred above that it belongs to triclinic, a = 9.7334, b = 9.2311 c = 10.4847 Å, α = 114.354, β = 87.951, δ = 71.422, volume = 798.113 $(Å)^3$ and density calculated as 3.541612 g/$cm^3$ with Z = 2.

In case of Hg $(NQO)_2$, the crystals belongs to triclinic with a = 12.4880, b = 11.5517, c = 6.2205 Å, α = $113.486^0$, β = 107.915 Å, = $81.917^0$, volume = 782.939 $(Å)^3$, density calculated 3.1810 g/$cm^3$ and Z = 2.

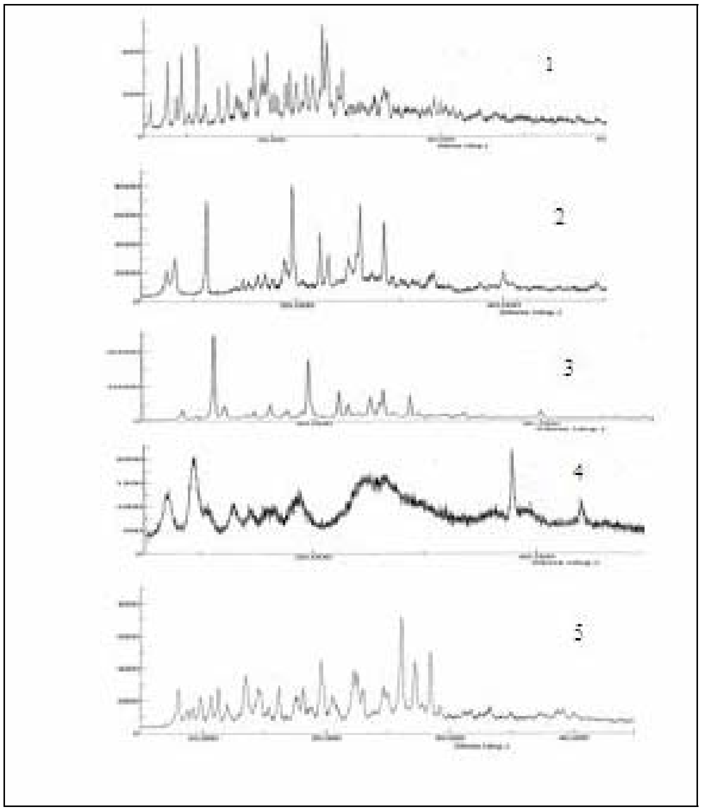

**Fig. 1: XRD Patterns of metal chelates (1) $Pb(NQO)_2$, (2) $Hg(NQO)_2$, (3) $Zn(NQO)_2$, (4) Ag(NQO) and (5) $Cd(NQO)_2$**

The particle size was calculated using Debye Scherer Formula and the values found to be for $Zn(NQO)_2$ as 33.48 nm and for $Hg(NQO)_2$ as 38.04 nm, which indicates that these crystals are nano crystals. Other chelates of $Pb(NQO)_2$, $Cd(NQO)_2$ and Ag(NQO) are crystallites in nature but their crystallographic analysis could not be done, only particle sizes were calculated and found to be 34.71 nm, 28.93 nm and 25.54 nm, respectively.

## Electronic spectra (UV-Vis)

The UV spectra of the ligand NQO and its metal chelates $M(NQO)_2$ where (M = Pb, Zn, Hg and Cd) were studied a dimethyl sulphoxide (DMSO) solution and the data is complied in Table 5. NQO exhibits absorption bonds at 213.2 nm and at 262.3 nm. These bonds are assigned to $\pi$ to $\pi^*$. The band at 262.3 nm is originated from the $\pi$ to $\pi^*$ of the orthoquinone oxime[12]. The chelates, studied here show only single transition at 262.1 nm which is $\pi$ to $\pi^*$ transition.

**Table 5: Electronic absorption data (λ nm) of metal chelates in DMSO in the range (200-800 nm)**

| Sr. No. | Compound | λ in nm | |
|---|---|---|---|
| **1** | (NQO) | 213.2 | 262.3 |
| **2** | Pb (NQO)2 | 212.1 | 261.1 |
| **3** | Zn (NQO)2 | 211.9 | 261.2 |
| **4** | Ag (NQO)2 | 212.1 | 261.1 |
| **5** | Hg (NQO)2 | 212.2 | 261.1 |
| **6** | Cd (NQO)2 | 212.5 | 261.2 |

## Infrared Spectra

IR frequencies of 1, 2-naphthoquinone 1-oxime were calculated by RHF / 6-31G* and reported by Jadhav et al.[13] In IR spectra of chelates $M(NQO)_2$ where M = Pb, Zn, Hg and Cd showed a weak V (C – H) stretching at about 3000 – 3400 $cm^{-1}$. The functional group such as C = O, C = N and N – O assigned. The data is given in Table 6. It can be seen from the table that the spectrum of NQO can be compared with chelates of metals which clearly shows lower wave numbers for V (C = N) and V (C = O) bands owing to elongation of these bonds upon coordination. The absorption of V (N – O) was found at higher wave numbers since this bond was significantly shortened in the chelates. The high position of V (NO) frequencies indicates that nitroso atom of the oxime group coordinates to the centre[14,15].

**Table 6: Characteristic IR ν ($cm^{-1}$) bands of NQO and its metal chelates**

| S. No. | Compound | O-H | C = O | C = N | N - O |
|---|---|---|---|---|---|
| **1** | NQO | 3527 | 1605 | 1698 | 1068 |
| **2** | Pb $(NQO)_2$ | 3064 | 1591 | 1620 | 1074 |
| **3** | Zn $(NQO)_2$ | 3342 | 1590 | 1617 | 1074 |
| **4** | Ag $(NQO)_2$ | --- | 1518 | 1618 | 1068 |
| **5** | Hg $(NQO)_2$ | 3325 | 1604 | 1620 | 1075 |
| **6** | Cd $(NQO)_2$ | 3325 | 1570 | 1620 | 1076 |

## Proton NMR

NQO gives chemicals shift at 9.24 and 9.22 ppm for N-OH group. The chemical shift for hydroxyl proton is not observed in the chelates of Ag, Zn and Cd. While Pb chelate exhibits chemical shift at 9.30 ppm and chelate Hg exhibits at 9.28 and 9.26 ppm and remaining chemical shifts are similar to ligand molecule[16,17].

$^{13}C$ NMR chemical shifts of $C_1$ and $C_2$ where –N- on l = is bonded. NQO exhibits chemical shifts at 147.74 and 182.64 and $CdCl_3$ for $C_1$ and $C_2$. The chemical shift for C1 is observed at 182 ppm for the chelates of Zn, Pb and Hg while the chemicals Ag and Cd are not appear. For $C_2$ the chemical shifts are shown at 147 ppm for all the chelates studied here. The chemical shifts of remaining carbons are in good agreement[18,19].

## Metal–organic frameworks

Crystalline porous coordination polymers (PCPs), also called metal–organic frameworks (MOFs), are a fascinating class of solid-state inorganic–organic hybrid materials. Research into these compounds is expanding very rapidly owing to their exciting combination of properties for advanced functional materials in gas storage and gas separation, catalysis, chemical sensing, as well as medical applications. Fig. 2 shows SEM of (1) NQO, (2) $Hg(NQO)_2$, (3) Ag(NQO), (4) $Pb(NQO)_2$, (5) $Zn(NQO)_2$ and (6) $Cd(NQO)_2$. Its synthesis involves the following steps

Metal ion + Organic linker ----- Nucleation ------ Crystal growth

The growth orientation [100] on the layer-by-layer growth of the same MOF requires the coordination through NQO-metal ion. This NQO-metal interaction, which forms the two-dimensional layer of the MOF, was impeded by the presence of oxime and hydroxyl group. Therefore, the selective coordination-modulation method enhanced the relative crystal growth in the [001] direction. The material grown under coordination modulation was significantly enhanced compared to that of the usually obtained microcrystalline powder of $M\text{-}(NQO)_2$. The growth of metal chelates is observesed as bulk crystals. The crystallite size of chelates is found to be nano range as 28.92 nm, 38.04 nm, 25.54 nm, 34.71 nm, 33.98 nm and 28.93 nm, respectively which is calculated using XRD data and Scherrer formula. This difference was attributed to the higher structural defects of the usual material as compared with the coordination-modulated nano-MOF. Nevertheless, direct evidence of coordinated oxime groups during crystallization in the framework as a powder has not been reported. Even more generally, the fabrication and characterization of well-defined, stable self-assembled monolayers (SAMs) of organic legends at a crystal face of a MOF has not been documented to date.

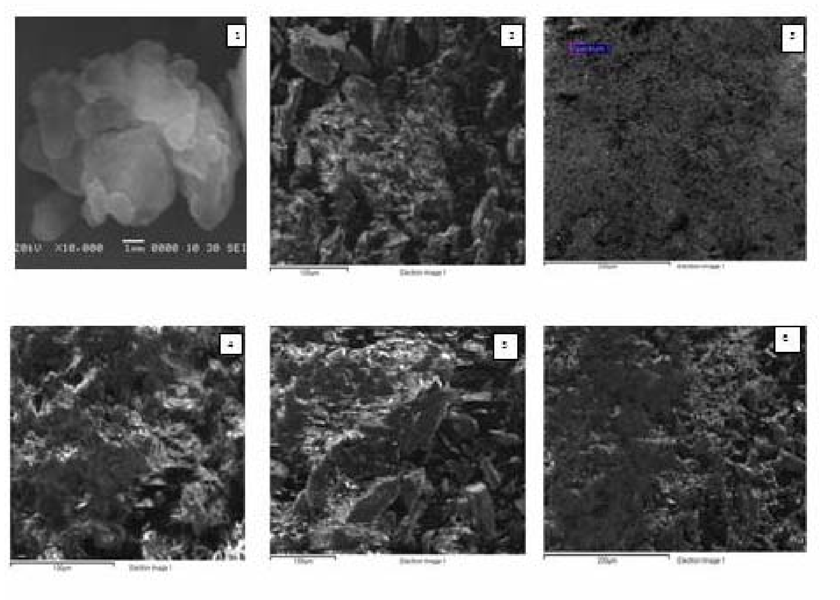

**Fig. 2: SEM data of (1) NQO, (2) $Hg(NQO)_2$, (3) Ag(NQO), (4) $Pb(NQO)_2$, (5) $Zn(NQO)_2$ and (6) $Cd(NQO)_2$**

## Liquid chromatography-Mass Spectra (LC-MS)

LC-MS of NQO was carried out and found that it gives retention time as 2.188 min. for 100%. It shows base peak for NQO m/Z at 173.85. Metal chelates of silver and cadmium of NQO shows base peak m/z at 173.95 for both and chromatographic retention time as 2.073 min.

## Antimicrobial scanning results

The NQO and its metal chelates were screened for their antimicrobial activities against *E. coli, B. subtilis, S. auerus, P. vulgaris, P. aeruginosa, A. niger and C. albicans*. The testing against growth of micro-organisms was carried out by using well diffusion method employing Mueller Hinton Agar (MHA) and culture in nutrient broth in each case of micro-organisms. The concentration of NQO and its metal chelates were chosen as $10^{-4}$ M. The plates were incubated at 35°C for 24 hours in incubator. The clear zone of inhibition of growth for the organism was measured in mm and the data is given in Table 7. Dimethyl sulphoxide i.e. solvent used shows no inhibition for all organisms under studies. NQO has shown highest activity for P. vulgaris as well as with remaining organisms. The other results are as follows:

(i) $Zn(NQO)_2$ showed good activity against all organisms and showed highest activity for S.aureus.

(ii) $Pb(NQO)_2$, Ag (NQO), Hg $(NQO)_2$ and Cd $(NQO)_2$ showed highest activity for *P. vulgaris*. The inhibition of the micro-organism growth for metal chelates was found to be in the following order.

$$Hg > Cd \geq Pb > Ag$$

The studies demonstrate that metal chelation can increase the anti microbial activity than metal free ligand. It is reported that metal chelation reduces the polarity of the metal ion mainly due to the partial sharing of its positive change with the donor group and possibly the δ electron decolization occurring within the whole chelate ring system formed during co-ordination and results in increase of the lipophilic nature of the central metal atom[20]. It favours for its penetration through the lipoid layer of the membrane.

The transition metal chelates possess high degree of inhibition which can be due to the greater number of δ electrons which increases the electrostatic filed around the metal ion.

**Table 7: Antimicrobial activities of 1, 2 naphthoquinone-1, oxime (NQO) and its metal chelates**

| Compd. | *E. coli* | *Bacillus subtilis* | *Staphy lococcus aureus* | *Proteus vulgaris* | *P. aeruginosa* | *A. niger* | *Candida albicans* |
|---|---|---|---|---|---|---|---|
| **DMSO** | Nil | Nil | Nil | Nil | Nil | Nil | Nil |
| **NQO** | 21.0 | 27.0 | 25.0 | 30.0 | 24.0 | 21.0 | 24.0 |
| **$Zn(NQO)_2$** | 22.0 | 24.5 | 22.0 | 21.5 | 22.0 | 26.0 | 26.0 |
| **$Pb(NQO)_2$** | 21.0 | 26.0 | 19.0 | 28.0 | 29.0 | 23.0 | 23.0 |
| **Ag(NQO)** | 21.0 | 24.5 | 21.0 | 25.0 | 24.0 | 26.0 | 24.0 |
| **$Hg(NQO)_2$** | 19.5 | 20.0 | 20.0 | 31.0 | 28.0 | 26.0 | 26.0 |
| **$Cd(NQO)_2$** | 19.0 | 23.5 | 21.0 | 28.0 | 26.0 | 24.0 | 24.0 |

(Inhibition zone diameter in mm)

## CONCLUSION

The metal chelates are thermally stable which a unique characteristic property is. All these chelates are crystalline in nature and generally belong to triclinic. The coordination ability of NQO towards M (II) chelates were examined by different spectroscopic methods that unequivocally determine the coordination sites of NQO. It is observed that the ratio of metal to NQO is 1 : 2 for chelates of Zn, Pb, Cd and Hg while in case of Ag the ratio is 1 : 1. This data is supported by LC-MS work. Biological activity screening proved the good antimicrobial activity of NQO and its metal chelates. The antimicrobial activity is explores on the bases of overtone concept of cell permeability.

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