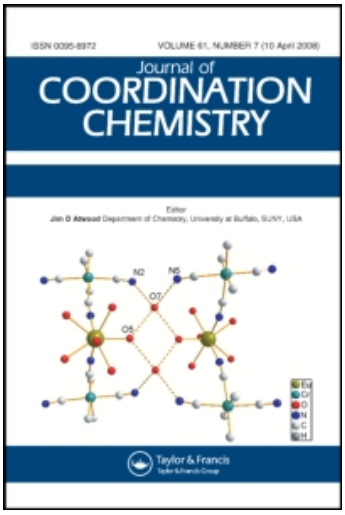


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# Synthesis, catalytic and antibacterial activity of 2-aminophenyldisulphide

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Metal complexes **1a–1c** have been synthesized using 2-aminophenyldisulphide, **1**, while **2d** and **2e** were synthesized from 2-hydroxybenzaldehyde phenyldisulphide diimine, **2**. All complexes were characterized by elemental analysis, spectroscopic data and magnetic moments. At room temperature complexes **1a**, **2a–2c** and **3b** catalyse the oxidation of primary alcohols and cyclohexene using NMO or $H_2O_2$ as co oxidant. The compounds **1–6** and some metal complexes were evaluated for their antibacterial activities against gram-positive and gram-negative bacteria.

*Keywords*: 2-Aminophenyldisulphide; Catalytic; NMO; $H_2O_2$; Antibacterial

## 1. Introduction

Research has been directed towards an understanding of the reactions of metal ions with ligands containing disulphide groups [1–3]. 2-Aminophenyl disulphide or diimine derivatives have been reported to give mononuclear or binuclear metal complexes and displayed diverse modes of coordination [4–8]. Many Schiff-base metal complexes have been reported to catalyse organic oxidations in the presence of co-oxidants such as $O_2$, $H_2O_2$, NMO, *t*-BuOOH and MCPBA [8–12]. Another important characteristic of Schiff bases is that they display antibacterial activity [13–15]. In our previous work, we reported the synthesis, catalytic and anti-bacterial activity of some ruthenium benzamide complexes [16, 17].

We undertook the present investigation with the objective of studying the catalytic activity of ruthenium diamine and diimine complexes towards primary alcohol, cyclohexene and tetrahydrofuran oxidation. We also herein report the antibacterial activity of some metal complexes of 2-aminophenyldisulphide, **1** and 2-substitutedbenzaldehyde phenyldisulphide, **2–4** (figure 1).

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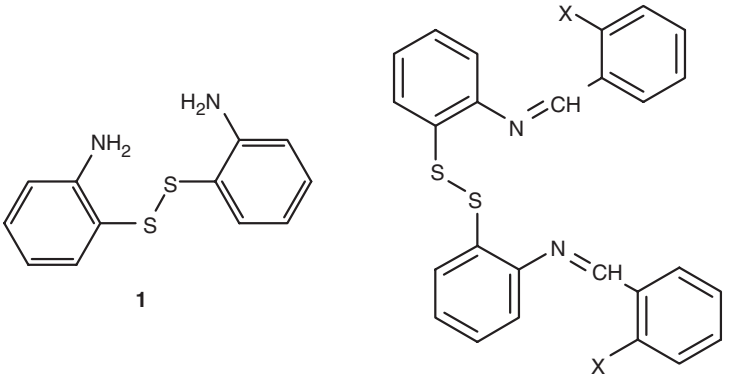


**1**: 2–aminophenyldisulphide

**2**: 2–hydroxybenzaldehyde phenyldisulphide (X = OH)

**3**: 2–chlorobenzaldehyde phenyldisulphide (X = Cl)

**4**: 2–nitrobenzaldehyde phenyldisulphide ($X = NO_2$)

Figure 1. Structure of ligands.



## 2. Experimental

The reagents $RuCl_3 \cdot 3H_2O$, $ZnCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$ and 2-aminophenyldisulphide were purchased from Aldrich or BDH and were used without further purification. Ethanol was distilled prior to use.

### 2.1. *Synthesis of metal complexes of 2-aminophenyldisulphide*

The metal chloride (0.6 mmol) was added to a solution of 2-aminophenyldisulphide (0.4 mmol) in methanol (30 $cm^3$) and refluxed for 4½ h. The obtained product was filtered, washed with methanol and diethylether and dried under vacuo.

**2.1.1. Trichloro aqua 2-aminophenyldisulphide ruthenium(III), (1a).** Black solid (yield: 55%). Anal. Calcd (found) for $RuC_{12}H_{14}N_2OS_2Cl_3$ (%): C, 30.3 (30.8); H, 2.9 (2.2); N, 5.9 (5.4); S, 13.5 (13.3); Cl, 22.5 (24.7).

**2.1.2. Dichloro aqua 2-aminophenyldisulphide zinc(II), (1b).** Off-white solid (yield: 60%). Anal. Calcd (found) for $ZnC_{12}H_{14}N_2OS_2Cl_2$ (%): C, 35.7 (36.0); H, 3.4 (3.4); N, 6.9 (7.5); S, 15.9 (16.4); Cl, 17.6 (19.0).

**2.1.3. Dichloro aqua 2-aminophenyldisulphide copper(II), (1c).** Black solid (yield: 70%). Anal. Calcd (found) $CuC_{12}H_{14}N_2OS_2Cl_2$ (%): C, 36.0 (37.0); H, 3.5 (3.6); N, 7.0 (6.9); S, 16.0 (16.4); Cl, 15.9 (15.1).

### 2.2. *Synthesis of metal complexes of 2-hydroxybenzaldehyde phenyldisulphide diimine, 2 Chloro 2-hydroxybenzaldehyde phenyldisulphide diimine copper(I) (2d)*

To a solution of salicyaldehyde (3.32 mmol) in ethanol (20 $cm^3$), a solution of 2-aminophenyldisulphide (1.66 mmol, 0.413 g) was added in ethanol (20 $cm^3$) and the reaction mixture was refluxed for 2 h. The Schiff-base ligand 2-hydroxybenzaldehyde phenyldisulphide diimine (0.94 mmol, 0.43 g), 2, formed was added to an ethanolic solution (30 $cm^3$) of $CuCl_2 \cdot 2H_2O$ (0.94 mmol, 0.16 g) and the reaction mixture was refluxed for 3 h. The resulting green solution was filtered, concentrated and precipitated with ether. The green solid obtained was washed and re-crystallised with ethanol (yield: 56%). Anal. Calcd (found) for $CuC_{26}H_{20}N_2O_2S_2Cl$ (%): C, 56.2 (56.5); H, 3.6 (3.7); N, 5.0 (5.1); S, 11.5 (12.8); Cl, 6.3 (7.1); Cu, 11.4 (12.5).

**2.2.1. Dichloro diaqua 2-hydroxybenzaldehyde phenyldisulphide diimine cobalt(II) (2e).** The above synthesised Schiff base 2-hydroxybenzaldehyde phenyldisulphide diimine (0.77 mmol, 0.35 g) was added to an ethanolic solution (30 $cm^3$) of $CoCl_2 \cdot 6H_2O$ (0.77 mmol, 0.18 g) and the resulting mixture was refluxed for 4 h. The resulting blackish green solution was filtered, concentrated and precipitated with diethyl ether. The obtained product was re-crystallized with ethanol and dried in vacuo (yield: 65%). Anal. Calcd (found) for $CoC_{26}H_{24}N_2O_4S_2Cl_2$ (%): C, 50.1 (49.6); H, 3.8 (3.2); N, 4.5 (3.8); S, 10.2 (10.3); Cl, 11.4 (12.8).



### 2.3. *Instrumentation*

Infrared spectra (KBr pellets) were recorded on an Avatar spectrometer in the range of 4000–400 $cm^{-1}$. UV-Visible spectra were recorded on a PU 8700 series UV-Visible spectrometer. $^1$H-NMR and $^{13}$C NMR spectra were recorded from a Bruker spectrospin-250. Magnetic susceptibility measurements of the complexes were performed at room temperature using a Sherwood Scientific magnetic balance. A LECO 932 CHNS Mattson 1000 spectrophotometer was used to collect microanalytical data (C, H, N, and S). The metal content was determined using Atomic Absorption Spectroscopy. Mass spectra were recorded on a thermo Finnigan ESI-Ion trap using methanol or acetonitrile as solvent.

### 2.4. *Procedure for catalytic studies*

**2.4.1. Oxidation of primary alcohols.** To a solution of the primary alcohol (1 mmol) in dichloromethane (20 $cm^3$), the co-oxidant NMO (3 mmol) and the complex (0.02 g) were added. The solution was stirred for 3 h at room temperature in the presence of molecular sieves. The mixture was filtered, evaporated to dryness and then extracted with diethylether ($2 \times 25$ $cm^3$). The ether extracts were combined and concentrated to give the corresponding aldehyde which was quantified as 2,4-dinitrophenylhydrazone.

**2.4.2. Oxidation of cyclohexene.** In a typical experiment, the metal complex (0.02 g) and substrate (45 mmol) were stirred in acetonitrile (10 mL) for 10 minutes in the presence of 30% $H_2O_2$ (1.53 $cm^3$, 50 mmol) under nitrogen at room temperature for 3 h.

Aliquots of the reaction mixture were then subjected to GC for analysis of the oxidation products at different time intervals (24 and 48 h). Gas chromatographic analyses were performed using the 610 Gas Chromatography (Pie-Unicam) instrument on a 30 m long DB-1 column with an FID detector. GC parameters were quantified by authentic samples prior to analysis.

**2.4.3. Oxidation of THF.** A similar procedure to that described for catalytic oxidation of cyclohexene was adopted. Dichloromethane was used as solvent.

### 2.5. *Statistical analysis*

Analysis of variance (ANOVA) was performed using a general linear model procedure for the antibacterial data. A randomized complete block design with repeated measurements was applied in this study. The significance of differences of the antibacterial value of four replicates was determined at the 95% confidence limit ($P = 0.05$).



## 3. Results and discussion

### 3.1. *Characterization of complexes*

When 2-aminophenyldisulphide was refluxed with $RuCl_3$, $ZnCl_2$ and $CuCl_2$, mononuclear complexes **1a–1c** were isolated (table 1).

The complexes **1a–1c** showed peaks at 3320–3430 $cm^{-1}$ (3380 and 3298 $\nu_{NH}$ in free ligand) and 1615–1618 $cm^{-1}$ (1613 $\delta_{NH}$ in free ligand) corresponding to the $NH_2$ stretching and bending modes, respectively, indicating coordination of the $NH_2$ with the metal. Complexes **1a–1c** exhibited a broad peak in the region 3500–3440 $cm^{-1}$

Table 1. Spectroscopic and magnetic susceptibility for complexes.

| Complex | IR ($cm^{-1}$) | UV-vis $\lambda_{max}$ ($e_{max}$, $M^{-1} cm^{-1}$) | $^1H$ NMR | $\mu_{eff}$ (BM) |
|---|---|---|---|---|
| **1a** | 3434, 1615, 757 | 228(9973)<br>291(19267)<br>560(5033) | | 1.3 |
| **1b** | 3419, 3220, 1615, 814 | 260(21840)<br>348(18233)<br>352(18307) | 5.4(s, 4H), 6.3–7.1(m, 8H) | – |
| **1c** | 3410, 3321, 1609, 824 | 252(11128)<br>258(18484)<br>524(2123) | | 1.7 |
| **2d** | 1622, 1589, 817 | 291(30663)<br>330(38947)<br>523(1298)<br>631(1265) | 7.0–8.2(m, 18H), 11.6(s, 2H) | – |
| **2e** | 1604, 749 | 265(39825)<br>401(13680)<br>617(4192) | | 1.6 |

–: Diamagnetic.

attributed to co-ordinated water molecules. In some cases the peak was merged with the NH stretching band. In the ligand **1**, the $\nu_{CS}$ appeared at 753 $cm^{-1}$. The new medium intense bands at 814 and 824 $cm^{-1}$ for **1b** and **1c** showed coordination of sulfur with the metal as reported in the literature [7]. The amine protons in **1b** shifted downfield compared to **1**.

When **2** was refluxed with $ZnCl_2$, $CuCl_2$, or $CoCl_2$, **2d** and **2e** were obtained while no zinc complex was formed which could be due to the size factor (table 1).

The IR spectrum of **2** showed imine peak at 1614 $cm^{-1}$ while its metal complexes **2d** and **2e**, displayed bands typical of co-ordinated Schiff base ligands at 1622 and 1604 $cm^{-1}$, respectively. The C–S mode of the Schiff base **2** at 752 $cm^{-1}$ shifted to higher frequency in **2d** indicating Cu–S linkage while no change was observed for **2e** showing no Co–S linkage. Complex **2e** exhibited a broad peak at 3500–3440 $cm^{-1}$ corresponding to coordinated water molecules.

The $^1$H NMR of **2d** (figure 2) showed a singlet at $\delta$ 11.6 ppm due to phenolic protons, confirming the non-coordination of the phenolic OH to the metal.

Electronic spectra of **2** in DMSO showed a broad band at 271 ($\varepsilon = 63{,}589$) and 351 ($\varepsilon = 51\,026$) nm attributed to $\pi$–$\pi^*$ and $n$–$\pi^*$ transitions. The electronic spectra of **2d** and **2e** in DMSO were characterized by charge transfer bands. Bands below 340 nm are intraligand charge transfer transitions while bands in the visible region are assigned to ligand to metal charge transfer. The bands (523 and 631 nm) in the visible region for **2d** were assigned to ligand to metal charge transfer, in conformity with square planar geometry [4].



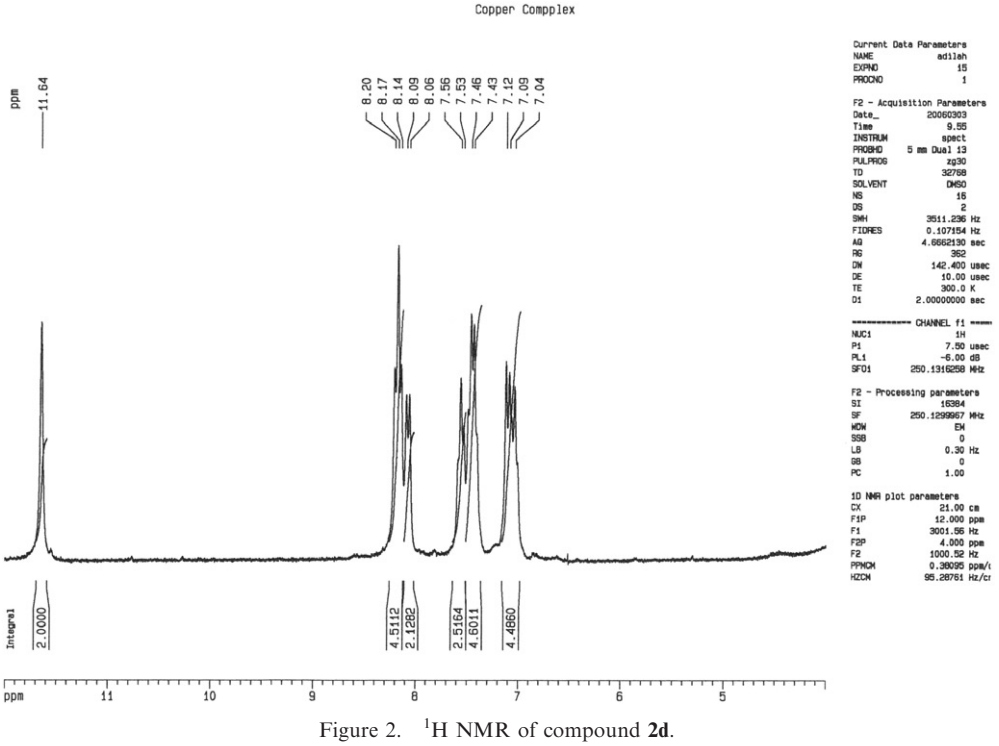


Figure 2. $^1$H NMR of compound **2d**.

However, Palanaindavar and coworkers reported $Cu(ClO_4)_2$ reacted with the sodium salt of **2** in the presence of $Et_3N$ to yield a product where deprotonation of hydroxyl protons was observed before coordination to the metal [4].

Compound **2d** was found to be diamagnetic indicating reduction of Cu(II) ($d^9$) to Cu(I) ($d^{10}$) and this was further confirmed by the mass spectral data. The mass spectrum of **2d** using electrospray showed a peak at 542 amu (after losing Cl ion) which corresponded to the sodium adduct with a formula $CuC_{26}H_{20}N_2S_2O_2$ while 538 amu ion was possibly the sodium adduct corresponding to the formula $CuC_{26}H_{16}N_2S_2O_2$. The pattern obtained for 538 indicated that **2d** contains one copper confirming the mononuclear structure. The other major fragments were 228 amu (hydrogen ion adduct of $C_{13}H_9SNO$), 200 amu ($C_{12}H_9SN$) and 186 amu ($C_{10}H_7SN$).

The reaction of $RuCl_3$ with 2-hydroxy benzaldehyde phenyldisulphide diimine, **2** in the presence of ligands $L$ ($L = 2,2'$-bipyridine, 1,10-phenanthroline or $PPh_3$) gave the binuclear complexes **2a–2c** while with 2-chlorobenzaldehyde phenyldisulphide diimine, **3** or 2-nitrobenzaldehyde phenyldisulphide diimine, **4** in the presence of 1,10-phenanthroline or $PPh_3$ gave the binuclear complexes **3b**, **3c** and **4b** [8]. We proposed earlier that in these complexes one of the ruthenium atoms is coordinated to one of the sulfur atoms as reported for similar types of complexes [6, 7]. The mass spectrum of complex **2a**, which was calculated by Finnigan's Excalibur Isotope Viewer showed the highest mass peak at 992.88 amu corresponding to a molecular formula of $C_{36}H_{32}O_4N_4S_2Cl_4Ru_2$, which confirmed the binuclear nature of the metal complex. This indicated that one ruthenium atom is coordinated to an imine nitrogen, one terminal chlorine, one bipyridine and two bridging chlorine atoms, while the other ruthenium is coordinated to the other imine nitrogen, one terminal Cl, two bridging Cl and two water molecules, instead of a sulfur coordination as we reported earlier [8]. The positive mass spectrum gave major fragments at $m/z$ 507 (sodium adduct of $RuCl_2(Bipy)_2$) and 489 ($C_{23}H_{19}N_3OClRu$) confirming the structure of **2a**.



### 3.2. *Catalytic oxidation*

The ability of complexes **1a**, **2a–2c**, **3b** and **3c** to catalyse the oxidation of various primary alcohols, cyclohexene and tetrahydrofuran was systematically examined in the presence of NMO, $H_2O_2$ or oxygen as the co-oxidant. Blank experiments revealed that no reaction occurred in the absence of either catalyst or the co-oxidant. All ruthenium compounds are active for oxidation; the oxidation results are compiled in tables 2 and 3.

Benzyl alcohol, allyl alcohol and cinnamyl alcohol were converted to their respective aldehydes. N-Donor ligand complexes **2a** and **2b** gave poorer yields for the oxidation of benzyl alcohol as compared to **2c**, while **2a** and **2c** gave comparable activity towards allyl alcohol and cinnamyl alcohol. When $H_2O_2$ or $O_2$ was used as co-oxidants, poorer yields were obtained.

A study of the recycling efficiency of **1a** using benzyl alcohol was undertaken. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with solvent and dried before using it in the subsequent run. It can be inferred that the catalyst can be recycled at least three times. However there was a progressive loss of activity accompanied by diminished yields (53–35%).

Table 2. Oxidations of primary alcohols using NMO as co-oxidant.

| Catalyst | Substrate | Product | Yield | Turnover |
|---|---|---|---|---|
| **1a** | Benzyl alcohol | A | 53 | 26 |
| | Cinnamyl alcohol | A | 61 | 29 |
| | Allyl alcohol | A | – | – |
| **2a** | Benzyl alcohol | A | 10 | 5 |
| | Cinnamyl alcohol | A | 56 | 87 |
| | Allyl alcohol | A | 58 | 32 |
| **2b** | Benzyl alcohol | A | 11 | 5 |
| | Cinnamyl alcohol | A | 53 | 84 |
| | Allyl alcohol | A | 60 | 30 |
| **2c** | Benzyl alcohol | A | 63 | 30 |
| | Cinnamyl alcohol | A | 60 | 94 |
| | Allyl alcohol | A | 60 | 38 |
| **3b** | Benzyl alcohol | A | 40 | 28 |
| | Cinnamyl alcohol | A | 74 | 56 |
| | Allyl alcohol | A | – | – |

A = Corresponding aldehyde.



Table 3. Oxidations of cyclohexene using $H_2O_2$ as co-oxidant.

| Catalyst | Substrate | Product | Hours | |
|---|---|---|---|---|
| | | | 24 | 48 |
| **1a** | Cyclohexene | Cyclohexene epoxide | – | – |
| | | Cyclohexene-1-ol | – | – |
| | | 2-Cyclohexen-1-one | – | – |
| **2a** | Cyclohexene | Cyclohexene epoxide | 0.3 | 1.0 |
| | | Cyclohexene-1-ol | 1.5 | 5.1 |
| | | 2-Cyclohexen-1-one | 1.5 | 5.7 |
| **2b** | Cyclohexene | Cyclohexene epoxide | 1.6 | 4.1 |
| | | Cyclohexene-1-ol | 2.4 | 6.7 |
| | | 2-Cyclohexen-1-one | 2.5 | 6.7 |
| **2c** | Cyclohexene | Cyclohexene epoxide | 1.3 | 1.2 |
| | | Cyclohexene-1-ol | 4.5 | 7.3 |
| | | 2-Cyclohexen-1-one | 4.1 | 8.0 |
| **3b** | Cyclohexene | Cyclohexene epoxide | 12.0 | 8.0 |
| | | Cyclohexene-1-ol | 1.4 | 6.7 |
| | | 2-Cyclohexen-1-one | 1.4 | 6.8 |

The formation of a Ru oxo species in the present work was supported by IR studies. IR spectra of the solid mass obtained by evaporation of the solution obtained by interacting the complex and NMO exhibited characteristic Ru oxo bands at 858 $cm^{-1}$, which disappeared after completion of reaction (3 h).

The complexes catalytically oxidize cyclohexene to a mixture of 2-cyclohexen-1-ol, 2-cyclohexene-1-one and cyclohexene epoxide over 24 and 48 h, with low yields. After 24 h, the percentage conversion to epoxide was more than the other two products. It was noted that after 48 h, the concentration of epoxide decreased while the yield of 2-cyclohexen-1-ol and 2-cyclohexene-1-one increased. It can be suggested that the epoxide formed first and then converted to the cyclohexen-ol and cyclohexene-one.

The complex **2a** catalyzed the oxidation of THF into $\gamma$-butyrolactone in 19% yield.

Complexes **1b**, **1c**, **2d** and **2e** did not show catalytic activity towards the oxidation of alcohols and hydrocarbons.

### 3.3. *Biological activity*

Diamine **1**, diimines **2–4**, carboxylate containing ligands (thiosalicylic acid **5**, dithiosalicylic acid **6**) and some ruthenium complexes **2a–2c**, **3b**, **3c**, **4b** [8] were screened for antibacterial activity against some Gram positive and Gram negative bacteria such as *Bacillus subtilus*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Salmonella typhi*, *Klebsiella pneumoniae* and *Proteus vulgaris* at different concentrations (1600, 800 & 100 $\mu g\,mL^{-1}$). The compounds containing sulfur and nitrogen atoms were more toxic to bacteria **1–3** as compared to those containing only sulfur and carboxylic groups, **5 & 6**. The presence of the imine group (>C=N–) was found to enhance the biological activity for both Gram positive and Gram negative bacteria strains tested [13]. However carboxylate containing compounds showed no significant activity against the strains tested except for *P. vulgaris*. The presence of the electron-withdrawing group – $NO_2$ (**4** & **4b)** considerably reduced the bactericidal effects of the compounds. However, while replacing OH by Cl comparable activity was observed. This similarity in activity may be due to the inductive effect caused by the two groups on the benzene ring, although Cl is an electron-withdrawing group, it can also donate electrons to the system by the mesomeric effect.

Ruthenium chelates have a slight increase in activity compared to the free ligands against the same microorganisms under similar experimental conditions (table 4). The presence of phenolphthalein in the complexes showed increase activity for Gram-positive bacteria.



Table 4. Antibacterial activity of ligands and their metal complexes.

| | | Diameter of zone of inhibition (mm) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | Conc $\mu g\,mL^{-1}$ | *B. subtilus* | *S. aureus* | *P. aeruginosa* | *E. coli* | *S. typhi* | *K. pneumoniae* | *P. vulgaris* |
| **1** | 800 | | **12** | | – | 10.5 | 10.5 | 1 |
| **2** | 1600 | 14 | 13 | 13 | 15 | 12 | 11 | 13 |
| | 800 | 13 | 12 | 11 | 14 | | | |
| | 100 | 10 | 10 | 10 | 10 | | | |
| **3** | 800 | | 13 | | | 12 | 11 | 13 |
| **4** | 800 | | 13 | | | – | – | – |
| **5** | 800 | | – | | – | – | – | 10 |
| **6** | 800 | | – | | – | – | – | 10 |
| **1a** | 800 | | 11 | | | 11 | 11 | 10 |
| **2a** | 1600 | 18 | 13 | 16 | 20 | 10 | 10 | 11 |
| | 800 | 14 | 12 | 12 | 15 | | | |
| | 100 | 12 | 10 | 11 | 12 | | | |
| **2b** | 1600 | 23 | 22 | 23 | 22 | 10 | 11 | 10 |
| | 800 | 18 | 16 | 14 | 14 | 10 | 10 | 10 |
| | 100 | 12 | 11 | 12 | 11 | | | |
| **2c** | 1600 | 15 | 15 | 15 | 14 | 13 | 12 | 15 |
| | 800 | 12 | 13 | 11 | 13 | 10 | 11 | 11 |
| | 100 | 10 | | 10 | 11 | | | |
| **3b** | 800 | | 13 | | – | 13 | 12 | 13 |
| | 100 | | 12 | | | 9 | 12 | 10 |
| **3c** | 800 | | 15 | | – | 12 | 13 | 15 |
| | 100 | | 11 | | – | – | – | – |
| **4b** | 800 | | 15 | | – | – | – | – |
| | 100 | | 11 | | | – | – | – |

The antibacterial values are significantly different ($P < 0.05$).
–: Inactive.

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