

## Synthesis and Characterization of Some Transition Metal Chelates of 2,2'-Dithiobenzoic Acid

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2,2'-Dithiobenzoic acid (**1**) metal complexes (**1a–4a**, **1b–4b**, **1c–4c**) were synthesized using **1** and metal salts such as copper(II), cobalt(II), manganese(II), nickel(II), zinc(II) acetates and ruthenium(III) chlorides in the absence or in the presence of diamines. The analytical and spectroscopic data of all complexes confirmed an octahedral geometry around the central metal ion with water molecules occupying the coordination sphere. Some of the metal complexes display antibacterial activity.

**Key Words:** Cu(II), Co(II), Mn(II), Ni(II), Zn(II), Ru(III), Chelates, 2,2'-Dithiobenzoic acid.

### INTRODUCTION

A literature search indicated that much research has been carried out on synthesis and characterization of carboxylate containing complexes.<sup>1–3</sup> The ability of carboxylate anions to work as bridging three-centre chelating ligands with M–M<sup>4–6</sup> bonds or without M–M<sup>7–9</sup> bonds is an attractive feature of this class of molecules employed mainly in the assemblage of di- and polymetallic units. The carboxylate metal chelates exhibit interesting biological activities<sup>10–12</sup> such as anti-inflammatory, antitumour, antimicrobial, anti-neoplastic and anticonvulsant properties. 2,2'-Dithiodisalicyclic (a disulphide ligand) with two potential coordination sites, has not been given much attention and therefore is the subject of the present work.

### EXPERIMENTAL

All chemicals were purchased from either Aldrich or BDH Chemicals and were used without purification with the exception of SOCl<sub>2</sub> and Et<sub>3</sub>N. Infrared spectra (KBr pellets) were recorded on a Mattson 1000 FT-IR spectrometer in the range 4000–400 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded on a Bruker spectrosin at 250 MHz. Carbon, hydrogen, nitrogen and sulphur contents were obtained using a LECO CHNS-932 analyser. The melting points of all samples was determined using a Stuart Scientific Electric melting point apparatus. Magnetic susceptibility data for the metal complexes was recorded on a Sherwood Scientific magnetic balance.

**Synthesis of metal complex (1a–6a):** 2,2'-Dithiobenzoic acid (1 mol) was

dissolved in 70 mL ethanol. To this solution, metal salt (1 mol) was added and the mixture was refluxed and stirred for 3 h. The solid obtained was filtered off, washed with hot ethanol and diethyl ether and dried under *vacuo*.

**Synthesis of metal complexes (1b–4b) and (1c–4c):** 2,2'-Dithiobenzoic acid metal salt and diamines were dissolved in about 70 mL of ethanol in a molar ratio of 1 : 1 : 1 and the resulting mixture was refluxed and stirred for 3 h. The solid obtained was filtered off, washed with hot ethanol and diethyl ether and dried under *vacuo*.

## RESULTS AND DISCUSSION

The metal complexes **1a–6a** were formed upon refluxing **1** with different metal salts such as Cu(II), Co(II), Mn(II), Ni(II) and Zn(II) acetates and ruthenium(III) chloride in a molar ratio of 1 : 1 in ethanol. When **1** and 1,2-phenylenediamine or 3,4-diaminotoluene and the different metal salts such as Cu(II), Co(II), Mn(II), Ni(II) and Zn(II) acetates and ruthenium(III) chloride were refluxed in a molar ratio of 1 : 1 : 1, complexes **1b–4b** and **1c–4c** were isolated. When **1**, diamine and Mn(II) acetate were refluxed, no coordination of diamines occurred and **3a** was isolated as confirmed by elemental analysis. Ruthenium trichloride in the presence of diamine and **1** yielded an impure compound. All the complexes were soluble in DMSO and insoluble in ethanol, water, diethyl-ether and chloroform. The analytical and spectroscopic data for all the complexes are reported in Table-1.

The infrared spectrum of the free ligand **1** showed a broad band at  $2987\text{ cm}^{-1}$  characteristic of  $\nu(\text{O—H})$  due to hydrogen bonding. The infrared spectra of the complexes **1a–6a** showed absence of the broad band at  $2987\text{ cm}^{-1}$  and presence of new bands in the region of  $3516\text{--}3415\text{ cm}^{-1}$  and around  $1582\text{--}1550\text{ cm}^{-1}$  indicative of asymmetric and symmetric  $\nu(\text{O—H})$  stretching and H—OH bending modes suggesting the presence of water molecules in the complexes. The carbonyl band present in the spectrum of the ligand ( $1680\text{ cm}^{-1}$ ) disappeared in that of metal complexes and was replaced by two bands at about  $1600\text{--}1590$  and  $1361\text{--}1407\text{ cm}^{-1}$  assignable to asymmetric and symmetric carboxylate stretching vibrations with the difference in wavenumbers suggesting unidentate bonding<sup>7</sup>.

The infrared spectra of the metal complexes **1b–4b** and **1c–4c** exhibited two sharp bands around  $3500\text{--}3200\text{ cm}^{-1}$  and *ca.*  $1500\text{ cm}^{-1}$  which corresponded to NH stretching and bending modes indicating the coordination of metal to the nitrogen of diamines. The carboxylic group stretching vibrations are found at  $1680\text{ cm}^{-1}$ , this being lowered in the case of metal complexes **1b–4b** and **1c–4c** showing coordination through the carboxylic groups. The infrared data of the metal complexes confirmed that the ligand undergoes prior deprotonation and then coordinates to the metal through its oxygen donor sites.

The  $^1\text{H}$  NMR spectra of diamagnetic complexes, **5a**, **6a**, **4b** and **4c**, recorded in DMSO- $d_6$ , showed presence of signals in the range 6.0 to 8.0 ppm indicative of aromatic protons. The absence of peaks at 12.6 ppm in all these complexes suggested deprotonation of the carboxylic groups and coordination through the carboxylate moiety of the ligand. For the metal complexes **4b** and **4c**, the  $\text{NH}_2$

protons appeared at  $\delta$  4.3 ppm indicating the presence of amine protons in the complexes. For the complex **4c**, the methyl protons were observed at  $\delta$  2 ppm.

The UV-visible spectra of metal complexes in DMSO showed intense bands around 300 nm assigned to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  charge transfer transitions. Bands in the region of 400–750 nm were assigned to ligand ( $\pi$ ) to metal (d) charge transfer or d-d transitions on the metal ions.

The metal complexes displayed magnetic moments corresponding to the presence of the unpaired electrons related to the divalent state of the metals in an octahedral environment. Zinc(II) complexes, **4b** and **4c**, were diamagnetic in accord with its  $d^{10}$  electronic configuration.

All the data confirmed that metal complexes possessed an octahedral geometry with water molecules in the coordination sphere.

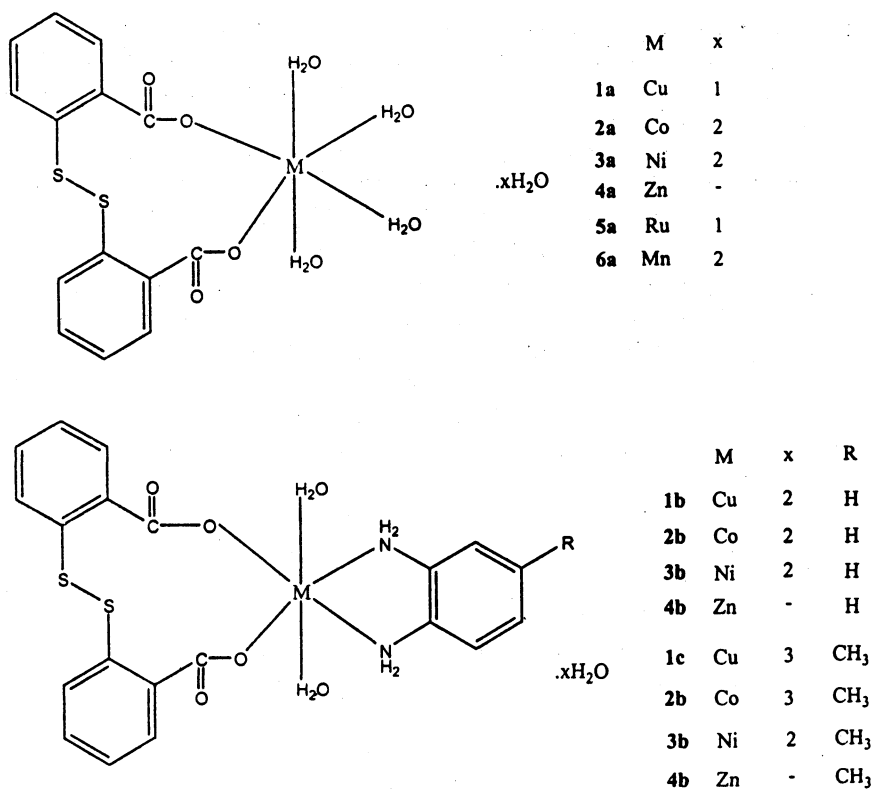


Fig. 1. Proposed structures of metal complexes

### Antibacterial activity

The synthesized complexes **1a–6a**, **1b–4b** and **1c–4c** have been screened for antibacterial properties against one gram-positive *Staphylococcus aureus* and three gram-negative bacteria, namely, *Escherichia coli*, *Salmonella typhi* and *Pseudomonas aeruginosa*, at a concentration of 1500  $\mu\text{g/mL}$  using DMSO as solvent. Blank tests, using DMSO, showed no growth of micro-organism.

TABLE-1  
ANALYTICAL, PHYSICAL DATA AND INFRARED SPECTRAL BANDS (cm<sup>-1</sup>) FOR  
THE METAL CHELATES OF 2,2'-DITHIOBENZOIC ACID

Compound	Yield (%)	Colour	m.p. (°C)	$\mu_{\text{eff}}$ (B.M.)	Found (Calc), %				$\nu_{\text{asy}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\nu(\text{O-H})$ $\nu(\text{N-H})$	$\delta(\text{H-OH})$
					C	H	N	S				
1a C <sub>14</sub> H <sub>18</sub> O <sub>9</sub> S <sub>2</sub> Cu	58	Dark green	> 300	0.98	36.8 (36.7)	4.0 (3.9)	—	13.6 (13.9)	1604	1400	3445	1580
2a C <sub>14</sub> H <sub>20</sub> O <sub>10</sub> S <sub>2</sub> Co	76	Purple	> 300	4.20	35.5 (35.6)	3.9 (4.2)	—	12.8 (13.1)	1590	1398	3442	1570
3a C <sub>14</sub> H <sub>20</sub> O <sub>10</sub> S <sub>2</sub> Ni	71	Light green	> 300	3.30	35.1 (35.6)	4.1 (4.2)	—	12.9 (13.5)	1590	1397	3423	1570
4a C <sub>14</sub> H <sub>16</sub> O <sub>8</sub> S <sub>2</sub> Zn	77	Cream	> 300	D	38.4 (38.1)	3.0 (3.6)	—	15.3 (14.5)	1596	1407	3516	1550
5a C <sub>14</sub> H <sub>18</sub> O <sub>9</sub> S <sub>2</sub> Ru	49	Dark purple	> 300	D	33.8 (33.9)	3.7 (3.6)	—	12.8 (12.9)	1600	1361	3415	1582
6a C <sub>14</sub> H <sub>20</sub> O <sub>10</sub> S <sub>2</sub> Mn	58	Brown	> 300	6.25	35.6 (35.9)	3.4 (4.3)	—	13.7 (13.7)	1600	1400	3421	1550
1b C <sub>20</sub> H <sub>24</sub> N <sub>2</sub> O <sub>8</sub> S <sub>2</sub> Cu	65	Greyish brown	> 300	1.88	43.3 (43.8)	4.0 (4.4)	5.0 (5.1)	10.6 (11.7)	1587	1384	3447	1575, 1546
2b C <sub>20</sub> H <sub>24</sub> O <sub>8</sub> N <sub>2</sub> S <sub>2</sub> Co	78	Purple	> 300	5.10	44.5 (44.2)	3.9 (4.4)	5.7 (5.2)	11.2 (11.7)	1606	1401	3400, 3327	1587, 1530
3b C <sub>20</sub> H <sub>24</sub> O <sub>8</sub> N <sub>2</sub> S <sub>2</sub> Ni	79	Greyish green	> 300	3.10	44.4 (44.2)	4.0 (4.4)	4.8 (5.1)	11.8 (11.7)	1614	1395	3466, 3276	1580, 1500
4b C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub> Zn	77	Cream	> 300	D	47.3 (46.8)	3.0 (3.6)	4.9 (5.4)	13.6 (12.5)	1592	1384	3443, 3245	1570, 1540
1c C <sub>21</sub> H <sub>28</sub> N <sub>2</sub> O <sub>9</sub> S <sub>2</sub> Cu	84	Greyish brown	285	1.83	43.8 (43.5)	3.9 (4.3)	5.2 (4.8)	11.0 (11.0)	1619	1369	3438, 3183	1590, 1505
2c C <sub>21</sub> H <sub>28</sub> N <sub>2</sub> O <sub>8</sub> S <sub>2</sub> Co	78	Brown	> 300	4.98	45.1 (45.2)	4.0 (4.6)	4.6 (5.0)	11.5 (11.5)	1589	1397	3419	1570, 1548
3c C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O <sub>7</sub> S <sub>2</sub> Ni	77	Greyish green	> 300	3.34	47.2 (46.8)	4.1 (4.5)	4.9 (5.2)	11.4 (11.8)	1635	1395	3422, 3250	1575, 1540
4c C <sub>21</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub> Zn	62	Off white	245	D	47.3 (47.9)	3.6 (3.8)	4.7 (5.3)	13.0 (12.2)	1587	1407	3440, 3363	1570, 1552

<sup>a</sup> KBr pellets, D = Diamagnetic.

Compound **2a** was active against all the four tested bacteria, while compounds **1a**, **3a–6a** were active against only *Pseudomonas aeruginosa*. In the presence of diamine (1,2-phenylenediamine or 3,4-diaminotoluene) ligands, the zinc complexes, **4b** and **4c** were found to be active against *Pseudomonas aeruginosa* and *Staphylococcus aureus* and the other metal complexes were inactive.

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