Complexing Ability of Some 2-Spirothiazolid-4-one Derivatives
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The complexes of some 2-spirothiazolid-4-one derivatives have been prepared with Cu(II), Ni(II), Co(II) and Cd(II) salts. The complexes all have a metal to ligand ratios of 1:1 or 1:2 and are all believed to have tetrahedral structures with chelating ligands. Their structures are suggested on the basis of analysis, X-ray diffraction techniques, spectral (UV–VIS, IR, 'H NMR), and thermal decomposition as well as conductivity measurements. The ligands are coordinated to the metal ions as monovalent bidentate ligands through the OCO groups. Electrical conductivity studies indicated that these complexes have activation energies in the range of semi-conducting materials. It is observed that some of the complexes are more potent as bacteriostatic agents than the free ligands.

Introduction
Thiazolidinone derivatives have considerable commercial importance as drugs [1–3] and herbicides [4]. Spiro compounds show photochromic properties, biological activity and optical activity [5–7]. Our interest in the coordination chemistry of biologically active compounds led us to study the ligating properties of some 2-spirothiazolid-4-ones whose coordination chemistry is not yet developed in the literature. We report in the present article the synthesis of Cu(II), Ni(II), Co(II) and Cd(II) chelates of some 2-spirothiazolid-4-one derivatives with the aim of investigating their biological activity. The complexes have been characterized by several tools in order to shed more light on the mode of bonding and structure of the prepared complexes.

The 2-spirothiazolid-4-ones used have the following structures:

![Structure I](image1)

![Structure II](image2)

I: 1-Thia-4-(2′-carboxyphenyl)azaspiro[4,5]decan-3-one (L1)
II: 1-Thia-4-(2′-carboxyphenyl)azaspiro[4,4]nonan-3-one (L2)

Experimental
All reagents used in this investigation were A.R. products (Merck or B.D.H.).

Synthesis, 1-thia-4-(2′-carboxyphenyl)azaspiro[4,5]decan-3-one (L1)
1-Oxa-4-thiaspiro[4,5]decan-2-one (1.58 g, 0.01 mol) was dissolved in 20 ml absolute ethanol. To this solution (1.3 g, 0.01 mol) ananthralic acid was added portionwise, and the mixture was refluxed for 1 h. The solvent was concentrated under reduced pressure and the reaction mixture was cooled to room temperature. L1 was precipitated as pale yellow crystals; yield: 2.43 g (95%); m.p. 105–107°C. C11H13NO5S
Calcd C 62.26 H 5.22 N 4.84 S 11.08%
Found C 62.40 H 5.10 N 5.10 S 11.20%

Synthesis, 1-thia-4-(2′-carboxyphenyl)azaspiro[4,4]nonan-3-one (L2)

This compound was prepared in an analogous manner from 1-oxa-4-thiaspiro[4,4]nonan-2-one; yield: 92% pale yellow crystals, m.p. 110–112°C. C11H13NO5S
Calcd C 61.07 H 4.75 N 5.08 S 11.64%
Found C 61.30 H 4.40 N 5.20 S 11.65%

Synthesis of the solid complexes
The following general procedure has been adopted for the preparation of the metal chelates. The required amount of the ligand was dissolved in the least amount of ethanol and treated with the appropriate amount of a solution of CuCl2·2H2O, NiCl2·6H2O, CoCl2·6H2O or CdCl2·2H2O in the molar ratio 1:1 and 2:1 (L:M). The mixtures were

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refluxed for about 1 – 3 h, evaporated to a small volume, and the solid complex that separated was filtered and then recrystallized from ethanol and dried in vacuo over preheated CaCl₂.

**Screening for antibacterial activity**

The antibacterial activity of the metal complexes was tested using the usual cup-plate diffusion technique [8, 9]. The culture media used are nutrient agar (NA) media supplemented with 1 g yeast per liter. A final concentration of 10 ppm of the test compounds was used. The data obtained are discussed below.

**Measurements**

Elemental analysis for C and H was carried out using a Perkin-Elmer 240 C instrument. The IR spectra were scanned on a Perkin-Elmer 599 B (4000 – 200 cm⁻¹) spectrophotometer by using the KBr disc technique. UV-VIS spectra were recorded on a CECIL 599 spectrophotometer using 1 cm matched silica cells. The metal analyses were performed by standard methods [10]. Thermogravimetric analysis was carried out in air with Du Pont Model 951, 910 and 1090 thermal analyzers at a heating rate of 10 °C min⁻¹. Conductivity measurements were carried out using a pye-bridge in DMF solution (10⁻⁴ M), and all the measurements were performed at ambient temperature (~25 °C).

For electrical conductivity measurements in the solid state, compressed pellets (1 cm² area) of 0.3–0.5 cm thickness were moulded at a pressure of 10 tons/cm². Two thin copper wires of diameter 25 mm were attached.

**Results and Discussion**

Analytical results and some physical properties of the chelates are listed in Table I. The results of elemental analyses (Table I) show that one and/or two molecules of the ligand are attached to the M(II) ion. Therefore three types of M(II) chelates are formed, having the formulae [MLCl₂H₂O], [ML₂H₂O][Cl and [M(L)₂], where L = L₁ or L₂, M = Cu(II), Ni(II), Co(II) or Cd(II). It is evident that L₁ and L₂ act as monobasic bidentate ligands through their carboxylic group. This behaviour is consistent with the coordination of these ligands to M(II) in their fully ionized form, a fact which is further supported by the IR and ¹H NMR spectra discussed below.

Molar conductance values of 10⁻⁴ M DMF solutions of the different chelates isolated are given in Table I. These indicate that all complexes are non-electrolytes except for the complexes 2, 4, 6 and 14 which have the values in the range of 1:1 electrolytes [11].

X-ray diffraction lines show that the positions and line intensities for the complexes 2, 4, 6 and 14 are similar, indicating that these complexes have the same configuration. Also, the complexes 3, 5, 7, 9, 11, 13 and 16 have similar configuration. This behaviour is further support for the formation of different types of complexes as mentioned before.

Coordination of water is revealed also from thermogravimetric analysis of the complexes 1, 2, 4, 6, 8, 10, 12 and 14 where a definite weight loss occurs between 160 and 190 °C corresponding to the presence of one or two coordinated water molecules except for the complexes 3, 5, 13 and 15 which do not show any weight loss up to 190 °C. Complexes containing lattice water molecules (cf. Table I) gave a weight loss at 100–130 °C.

**IR and ¹H NMR spectral studies**

The IR group frequencies of diagnostic importance are collected in Table II. The free ligands comprised a strong band at 1715 and 1675 cm⁻¹ of L₁ and L₂, respectively, which can be assigned to the stretching vibration of the carboxyl group belonging to the carboxyl function [12]. This band has completely disappeared in the spectra of the metal(II) chelates indicating coordination of the carboxylate groups, and instead two bands appear in the regions 1555–1590 and 1445–1460 cm⁻¹. These two bands are assignable to the asymmetric and symmetric stretching of the carboxylate group, respectively [12, 13]. The separation (νas-νs) of the carboxylate stretching vibrations and their relative intensity agree well with a carboxylate group coordinating in its bidentate mode [14, 15]. The distinct band appearing at 1630 and 1650 cm⁻¹ of all complexes could be attributed to the free νCO group belonging to the free ligands L₁ and L₂, respectively.

The presence of coordinated and lattice water molecules in the metal complexes has been confirmed by the new band appearing at 3260–3420 cm⁻¹ in the IR spectra of the complexes (cf. Table II). Also, the rocking mode of coordinated water molecules appeared as a weak vibra-...
Table I. Analytical and physical data of the metal complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Color</th>
<th>(E_a) (eV)</th>
<th>(A_{\infty}) ohm(^{-1}) cm(^2) mol(^{-1})</th>
<th>Calcd (Found) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{Cu}(\text{C}<em>{15}\text{H}</em>{14}\text{NSO}_3)\text{ClH}_2\text{O}]\text{H}_2\text{O})</td>
<td>green</td>
<td>0.49</td>
<td>15.10 (42.60)</td>
<td>42.55 (42.60)</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Ni}(\text{C}<em>{15}\text{H}</em>{14}\text{NSO}_3)_2\text{H}_2\text{O}]\text{Cl})</td>
<td>blue</td>
<td>0.37</td>
<td>70.00 (43.50)</td>
<td>43.40 (43.50)</td>
</tr>
<tr>
<td>3</td>
<td>([\text{Ni}(\text{C}<em>{15}\text{H}</em>{14}\text{NSO}_3)_2]) yellow</td>
<td>yellow</td>
<td>0.30</td>
<td>10.20 (56.50)</td>
<td>56.71 (56.50)</td>
</tr>
<tr>
<td>4</td>
<td>([\text{Co}(\text{C}<em>{15}\text{H}</em>{14}\text{NSO}_3)_2\text{H}_2\text{O}]\text{Cl})</td>
<td>dark key</td>
<td>0.30</td>
<td>80.20 (42.70)</td>
<td>43.02 (42.70)</td>
</tr>
<tr>
<td>5</td>
<td>([\text{Co}(\text{C}<em>{15}\text{H}</em>{14}\text{NSO}_3)_2]) green</td>
<td>green</td>
<td>0.29</td>
<td>7.30 (56.80)</td>
<td>56.68 (56.80)</td>
</tr>
<tr>
<td>6</td>
<td>([\text{Cd}(\text{C}<em>{15}\text{H}</em>{14}\text{NSO}_3)_2\text{H}_2\text{O}]\text{Cl})</td>
<td>yellowish</td>
<td>0.26</td>
<td>65.30 (37.70)</td>
<td>38.15 (37.70)</td>
</tr>
<tr>
<td>7</td>
<td>([\text{Cd}(\text{C}<em>{15}\text{H}</em>{14}\text{NSO}_3)_2]) yellow</td>
<td>yellow</td>
<td>0.25</td>
<td>12.40 (51.20)</td>
<td>50.95 (51.20)</td>
</tr>
<tr>
<td>8</td>
<td>([\text{Cu}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)\text{ClH}_2\text{O}]\text{H}_2\text{O})</td>
<td>dark-brown</td>
<td>0.46</td>
<td>16.30 (43.10)</td>
<td>42.97 (43.10)</td>
</tr>
<tr>
<td>9</td>
<td>([\text{Cu}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)_2\text{H}_2\text{O}]) brown</td>
<td>brown</td>
<td>0.42</td>
<td>10.20 (51.80)</td>
<td>51.88 (51.80)</td>
</tr>
<tr>
<td>10</td>
<td>([\text{Ni}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)\text{ClH}_2\text{O}_2]) blue</td>
<td>blue</td>
<td>0.39</td>
<td>14.30 (41.70)</td>
<td>41.57 (41.70)</td>
</tr>
<tr>
<td>11</td>
<td>([\text{Ni}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)_2]) blue</td>
<td>blue</td>
<td>0.35</td>
<td>6.10 (57.52)</td>
<td>57.52 (57.52)</td>
</tr>
<tr>
<td>12</td>
<td>([\text{Co}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)\text{ClH}_2\text{O}]) brown</td>
<td>brown</td>
<td>0.33</td>
<td>12.30 (43.50)</td>
<td>43.48 (43.50)</td>
</tr>
<tr>
<td>13</td>
<td>([\text{Co}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)_2]) brown</td>
<td>brown</td>
<td>0.32</td>
<td>25.10 (55.50)</td>
<td>55.35 (55.50)</td>
</tr>
<tr>
<td>14</td>
<td>([\text{Cd}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)_2\text{H}_2\text{O}]\text{Cl}) yellow</td>
<td>yellow</td>
<td>0.21</td>
<td>75.20 (36.70)</td>
<td>36.69 (36.70)</td>
</tr>
<tr>
<td>15</td>
<td>([\text{Cd}(\text{C}<em>{14}\text{H}</em>{12}\text{NSO}_3)_2]) yellow</td>
<td>yellow</td>
<td>0.18</td>
<td>8.20 (51.00)</td>
<td>50.87 (51.00)</td>
</tr>
</tbody>
</table>

The metal-ligand vibrations are expected below 600 cm\(^{-1}\), and they offer means for correlating the stability order of the metal complexes and the strength of the M – O bond. The presence of bands between 405 and 440 cm\(^{-1}\) has been suggested by some workers [17] to be due to bonding to metal through the oxygen atom of the ligand.

The \(^1\)H NMR spectra of the free ligands show signals at 11.6 (L\(_x\)) and 10.79 (L\(_2\)) ppm assigned to the free OH proton of the carboxyl group. The OH signals are absent in the spectra of all the metal complexes, confirming deprotonation. These observations together with elemental analyses, and IR spectral studies confirm that the two free ligands react with metal(II) ions through the carboxylic groups with loss of a proton (from the OH group) thus creating bidentate mononegative ligands.

Electronic spectra

The electronic absorption spectra of DMF solutions of the free ligands and their complexes have been recorded in the wavelength range 300 – 800 nm. \(\lambda_{\text{max}}\) values of the different absorption bands displayed by the complexes are given in Table II. From the electronic spectra some general features can be recognized:

All the complexes comprise a broad composite band in the visible region. This band exhibits mainly two maxima, the first in the wavelength range 360 – 390 nm being due to intraligand transitions,
Com pound

Free L

Cu - L

Ni - L

Ni - 2 L

Co - L

Co - 2 L

Cd - L

Cd - 2 L

Free L

Cu - L

Cu - 2 L

Ni - L

Ni - 2 L

Co - L

Co - 2 L

Cd - L

Cd - 2 L

Table II. IR and electronic spectra of the free ligands and solid complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Assignment [cm⁻¹]</th>
<th>vOH</th>
<th>vC=O</th>
<th>v_s OCO</th>
<th>v_1 OCO</th>
<th>vM-O</th>
<th>λ_max [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu - L</td>
<td>3300</td>
<td>1715</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>360, 395, 450</td>
</tr>
<tr>
<td>Ni - L</td>
<td>3260</td>
<td>1555</td>
<td>1455</td>
<td>415</td>
<td>-</td>
<td>-</td>
<td>360, 390, 480, 560</td>
</tr>
<tr>
<td>Ni - 2 L</td>
<td>3420</td>
<td>1585</td>
<td>1450</td>
<td>415</td>
<td>-</td>
<td>-</td>
<td>360, 390, 475, 560</td>
</tr>
<tr>
<td>Co - L</td>
<td>3420</td>
<td>1590</td>
<td>1460</td>
<td>440</td>
<td>-</td>
<td>-</td>
<td>360, 390, 460, 530</td>
</tr>
<tr>
<td>Co - 2 L</td>
<td>3400</td>
<td>1590</td>
<td>1460</td>
<td>415</td>
<td>-</td>
<td>-</td>
<td>360, 390, 460, 530</td>
</tr>
<tr>
<td>Cd - L</td>
<td>3420</td>
<td>1585</td>
<td>1450</td>
<td>415</td>
<td>-</td>
<td>-</td>
<td>360, 390, 480</td>
</tr>
<tr>
<td>Cd - 2 L</td>
<td>3400</td>
<td>1595</td>
<td>1455</td>
<td>430</td>
<td>-</td>
<td>-</td>
<td>370, 390, 480</td>
</tr>
</tbody>
</table>

and the second in the range 390-480 nm attributable to an LMCT transition.

Cu(II), Ni(II) and Co(II) complexes exhibit characteristic d–d bands. Cd(II) complexes do not show any d–d bands, and their spectra are dominated only by charge transfer and ligand bands. Cu(II) complexes show a broad band at ca. 560 nm indicative of a tetrahedral structure of these complexes. The bands are assigned to d–d electronic transitions of the type ²E_g ← ²T_2g [18]. Co(II) complexes on the other hand show a broad band at ca. 530 nm. This band is due to a d–d electronic transition and lies in the range reported for four coordinate Co(II) complexes. Thus for the present Co(II) complexes this band corresponds to the ⁴A_2 → ⁴T_1(3p) transition [18]. Spectral data for the Ni(II) complexes (625–715 nm) indicate a tetrahedral stereochemistry through their ³T_1 → ³T_1(3p) transitions [18].

Electrical conductivities

The electrical conductivities (ρ) in ohm⁻¹ cm⁻¹ and the activation energies (ΔE) in eV of the free ligands and of their Cu(II), Ni(II), Co(II) and Cd(II) complexes were obtained by applying: ρ = ρ₀ exp⁻ΔE/kT. The results show that the ρ-values increase with increasing temperature obeying the usual behaviour of an intrinsic semiconductor. The activation energy (Ea) was obtained from a plot of lnρ against 1/T. The values of the activation energies were calculated using the least squares method. The results are given in Table I. These data show that the activation energy values decrease slightly on going from Cd(II) to Cu(II) complexes. Furthermore, the bicomplexes have lower conductivities and activation energies than the monocomplexes.

Antibacterial activity

The data obtained indicate the cases where the complexes show ambient bacteriostatic activity against *C. tropicalis*, *Pseudomonas floureuseus*, *Bacillus cereus*, *Serratia*. The antimicrobial activity of the complexes is higher than that of the free ligands. The antibacterial activity of the complexes against *Pseudomonas floureuseus* and *Bacillus cereus* decrease in the order: Cu < Co < Cd < Ni, and the effect is similar with *Serratia* and *C. tropicalis*. 