Spectral studies of Nickel(II) and Chromium (III) complexes with some organic acids in aqueous solution

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Abstract
Complexes of Cr(III) and Ni(II) ions with phthalate, sulphanilate, anthranilate, hippurate, 8-quinolinolate and glycinate ions have been prepared, absorption spectra of their aqueous solutions at the visible and U.V. region were recorded, then the Nephelauxetic ratio (B) was calculated. Results showed that covalency between metal ions and ligands is largely affected by π - bonding due to t2g electrons, the ligands could be arranged according to their increased tendency for covalent bonding (hig) as follows:
H2O < sulph < phth < Anth < 8-quo < Hipp < Gly.
Also Jorgensen's ligand field parameter (f_{lig}) was calculated and the ligands could be arranged according to their ligand field splittings as follows:
8-quo < H2O < Anth < Hipp < Phth < gly < sulph

Introduction
In the free atom or ion, measures of the energy separations of the various Russell-Saunders states are the Racah parameters (B) and (C).
In complexes, measures of the energy separation of states of the same spin multiplicity have energy differences multiples of (B), and for states of different multiplicity are expressed as sums of multiples of both (B) and (C). (B) is less than (B) of the free ion and (C) is less than (C) of the free ion too since spin-orbit interaction is greater in the case of free ion while it diminishes when complexing is taking place where electron delocalization is operated between metal ion and ligands. It is generally believed that expansion of the metal's (d) electron clouds occur because of the overlapping with ligand donor-atom orbitals, thus providing paths by which (d) electrons can escape from the metal ion. This effect of ligands in expanding the (d) electron clouds has been named the nephelauxetic effect; and it has been found that the common ligands can be arranged in order of their ability to cause cloud expansion, this order is independent of the metal ion. It is in part:

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F<sub>−</sub>H₂O<sub>−</sub>NH₃<sub>−</sub>Oxalate<sub>−</sub>en<sub>−</sub>NCS<sub>−</sub>Cℓ<sup>−</sup>CN<sup>−</sup>Br<sup>−</sup>I<sup>−</sup>.

The positions of the various metal ions according to their covalent tendencies with respect to bond formation as expected from the view point of "polarization" forces causing large distortion of the ligand's electronic structures are approximately.

Mn(II)<Mn(II)<V(II)<Fe(III)<Cr(III)<
Co(III)<Mn(III)<Rh(III)<Ir(III)<Pt(IV)

Nephelauxetic series are quite useful to the chemist since they may enable him to confirm or deny the presence of some complex species in solution merely from a knowledge of the spectra of other similar complexes, one such use is the distinction between cis and trans isomers. Another use is the easy recognition between complexes of the [Co(NH₃)₃NO₂]<sup>2+</sup> type which are either red when the linkage is M-O, or yellow when M-N bonding is involved. In the present research attempts were made firstly to study the nephelauxetic effect of certain organic ligands on (d) electron clouds of chromium(III) and nickel (II) metal ions, secondly to evaluate Jorgensen's ligand field splittings exerted by these ligands.

Experimental
Materials
All chemicals used were of B.D.H. analar grade.

Metal complexes
Metal perchlorate solutions in water were mixed with ligand solutions in water in the ratio (1:3), the temperature was raised to 60°C and maintained for period of one hour, then the solutions were cooled in an ice bath, the metal complex crystals were separated, dried in a desiccator, analysed for metal ions, ligands and water of hydration in the usual procedures.

Apparatus
Schemitz (U.V- vis ) recording spectrophotometer equipped with quartz cells were used in all measurements.

Results and Calculations
Electronic spectra in the visible and ultraviolet region of metal complexes and of pure ligand solutions were recorded and all transitions were assigned as can be seen in tables. I, II, and III. Values of the mixing factor (X) and of the racah parameter of the complexes were computed from the relations:

\[ v_1 - 1087 \quad v_2 - 1187 \quad v_3 - 11287 \quad 135 \quad h \]

the ratio \( \frac{v_1}{v_2} \) which is known as the nephelauxetic ratio \( \beta \) is useful in determining the nephelauxetic parameter \( K_M \) of the metal ion and the nephelauxetic parameter \( h_s \) of the ligand according to the equation:

\[ (1 - \beta) = K_M \cdot h_S \] (I)

\( \beta \) values are known for many metal ions in the free state. They are 918 cm<sup>−1</sup> for Cr<sup>3+</sup> and 1030 cm<sup>−1</sup> for Ni<sup>2+</sup>. \( \beta \) values of the complexes could be calculated from the energy level diagrams of the metal ions under different symmetries. For the d<sup>3</sup> and d<sup>8</sup> systems under investigation, the energy level diagram is represented by figure (3) for both ions.

From the ligand field splitting (10 Dq) obtained experimentally it is possible to compute Jorgensen's parameters of the organic ligands by using the relation:

\[ 10Dq = g_{on} \cdot h_{ig} \] (2)

where \( g_{on} \) and \( h_{ig} \) are the field factors of the metal ions and the ligands respectively. Values of these factors for the various ligands could be seen in table (III). Representative absorption spectra are given in figure (1) and figure (2) where aquated ions represent weak field case and sulfonated ions represent strong field case.
Discussion
Electronic spectra of chromium (III) complexes
Chromium (III) is the stablest oxidation state of the element where the energy level \( t_{2g} \) being half filled, octahedral complexes are the most common in chromium (III) compounds, the electrotransitions in the aquo complexes are\(^{(3)}\):
\[
\begin{align*}
\tilde{\nu}_1 & \quad [A_{2g} \rightarrow T_{2g}(F), \text{7,400 cm}^{-1}] \\
\tilde{\nu}_2 & \quad [A_{2g} \rightarrow T_{1g}(F), \text{24,700 cm}^{-1}] \\
\tilde{\nu}_3 & \quad [A_{2g} \rightarrow T_{1g}(P), \text{37,000 cm}^{-1}] 
\end{align*}
\]

Electronic spectra of Nickel (II) complexes
The presence of absorption band at 10,000 cm\(^{-1}\) in nickel complexes is an indication that the complexes are of octahedral symmetry, and not square planar one. On the other hand, the characteristic absorptions in tetrahedral complexes are three bands related to the transitions\(^{(3)}\):
\[
\begin{align*}
3^3T_2(F) & \rightarrow 3^3E(F) \\
3^3T_1(F) & \rightarrow 3^3A_1(F) \\
3^3T_1(F) & \rightarrow 3^3T_1(F)
\end{align*}
\]
since the crystal field splitting (Dq) in tetrahedral symmetry is 4/9 (Dq,6) of that of octahedral one, therefore absorptions are shifted towards the infra red region compared to absorption in octahedral symmetry and consequently it appears as a broad band at 15,000 cm\(^{-1}\) representing transitions \( 3^3T_1(P) \leftrightarrow 3^3T_1(F) \) and a weak band at either side of the latter band representing the spin forbidden transitions, also it shows absorption band at 7,000 cm\(^{-1}\) related to transitions \( 3^3A_2 \leftrightarrow 3^3T_1(F) \), the third band which represents the transitions \( 3^3T_1(F) \leftrightarrow \)

\( ^3T_1(P) \) disappears in tetrahedral complexes\(^{(3)}\).

Six coordinated complexes of Nickel (II) having a high spin electronic states are of octahedral symmetry. The two terms \( ^3F \) and \( ^3P \) resulting from the 3d\(^6\) configuration will suffer splitting as can be seen in fig(4) the expected three transitions are\(^{(3)}\):
\[
\begin{align*}
\tilde{\nu}_1 & \quad [3^3A_2 \rightarrow 3^3T_{2g}(F), \text{7,000--13,000 cm}^{-1}] \\
\tilde{\nu}_2 & \quad [3^3A_2 \rightarrow 3^3T_{1g}(F), \text{14,000--28,000 cm}^{-1}] \\
\tilde{\nu}_3 & \quad [3^3A_2 \rightarrow 3^3T_{1g}(P), \text{19,000--28,000 cm}^{-1}]
\end{align*}
\]
delocalization of (d) electrons of the metal ion is affected by two factors, firstly, the nature of the (d) electrons, whether they are of \( t_{2g} \) or \( e_g \) type, since in an octahedral environment \( e_g \) electrons are directed towards the ligands while \( t_{2g} \) electrons are directed between the ligands orbitals, whether they are empty or filled. In this research we do have a case where the metal ion possesses both \( t_{2g} \) and \( e_g \) electrons (case of \( \text{Ni}^{2+} \) ion) also we have a metal ion possesses \( t_{2g} \) electrons only (case of \( \text{Cr}^{3+} \) ion) in general low (b) values obtained for \( \text{Cr}^{3+} \) complexes is an indication of extensive delocalization of (d) electrons\(^7\), while high (b) values for \( \text{Ni}^{2+} \) complexes is a consequence of less delocalization of (d) electrons\(^8\).organic ligands used for complexation in this research have different characters ranging from bidentated having two anionic groups, i.e. phthalate on one hand forming sigma bonds to a bidentates on the other hand having one electron releasing and one anionic groups forming dative and sigma bonds respectively, i.e. sulfanilate, glycinate, 8-quinolinate, anthranillate and hippurate. From the values of \( h_{\text{lig}} \), the nephelauxetic parameter of the
ligand in table (II) it is possible to arrange the ligands according to their tendencies in forming covalent bonds with metal ions as follows:

H_2O < sulph < phth < Anth < 8-quin < Hipp < gly

The magnitude of the ligand field splitting (10Dq), as can be seen from equation (2), depends on two factors, namely, the nature of the metal ion (\(g_{\text{ion}}\)) and the nature of the ligand (\(f_{\text{lig}}\)). From the results of table (III), it is possible to arrange the ligands according to their influence in splitting the energy levels of the metal ions in complexes taking Jorgensen field factor (\(f_{\text{lig}}\)) as a measure for this tendency as follows:

8-quin < H_2O < Anth < Hipp < Phth < gly < sulph

Finally, the quantitative study of electron delocalization is only just beginning, it is to be hoped that when more spectral studies and other studies are reported and their interpretation is made more reliable it will be possible to translate many of our qualitative ideas about covalency into semi-quantitative statements about electron distribution and delocalization energy.

### Table (I)

**Absorption spectra of 0.06 M solution of ligands**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>KHP</th>
<th>Phthalamidequinidine</th>
<th>Antinucleic Acid</th>
<th>Sulphonucleic Acid</th>
<th>Gly</th>
<th>Hippionic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Waveno.</strong></td>
<td><strong>KHP</strong></td>
<td><strong>Phthalamidequinidine</strong></td>
<td><strong>Antinucleic Acid</strong></td>
<td><strong>Sulphonucleic Acid</strong></td>
<td><strong>Gly</strong></td>
<td><strong>Hippionic Acid</strong></td>
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<tr>
<td>1</td>
<td>9133.9</td>
<td>10235.4</td>
<td>10235.4</td>
<td>10235.4</td>
<td>10235.4</td>
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<tr>
<td>2</td>
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<td>11222.6</td>
<td>11389.5</td>
<td>11628.5</td>
<td>11750.8</td>
<td>11386.2</td>
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<tr>
<td>3</td>
<td>17857.1</td>
<td>27100.2</td>
<td>15348.7</td>
<td>15348.7</td>
<td>15348.7</td>
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</table>

### Table (II)

**Assignments of absorption bands and Nephelauxetic parameters**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(\nu_{1}^{\text{cm}^{-1}})</th>
<th>(\nu_{2}^{\text{cm}^{-1}})</th>
<th>(\nu_{3}^{\text{cm}^{-1}})</th>
<th>(\delta_{1})</th>
<th>(\delta_{2})</th>
<th>(\delta_{3})</th>
<th>(h_{\text{a}})</th>
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<tbody>
<tr>
<td>KHP</td>
<td>17271.1</td>
<td>17980.8</td>
<td>2859.9</td>
<td>230.7</td>
<td>6.705</td>
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<td>8615.7</td>
<td>11586.9</td>
<td>2544.5</td>
<td>189.7</td>
<td>0.833</td>
<td>1.01</td>
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<td>40066.3</td>
<td>446.20</td>
<td>0.492</td>
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<td>3550.8</td>
<td>2516.0</td>
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<td>6.625</td>
<td>2.70</td>
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<td>1906.0</td>
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<td>0.189</td>
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<tr>
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<td>10224.9</td>
<td>15530.1</td>
<td>25757.5</td>
<td>563</td>
<td>0.546</td>
<td>3.78</td>
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<tr>
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<td>21644.4</td>
<td>36520.0</td>
<td>385</td>
<td>0.42</td>
<td>2.9</td>
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<td>15726.5</td>
<td>24806.9</td>
<td>620</td>
<td>0.184</td>
<td>3.80</td>
<td></td>
</tr>
</tbody>
</table>

\(f = \beta \cdot \gamma\) where \(\nu_{\text{a}} = 1030 \text{ cm}^{-1}\) and \(\gamma = 918 \text{ cm}^{-1}\)

\((1-\beta) = h_{\text{a}} = K_{\text{a}}\) where \(K_{\text{a}} = 0.12\) and \(\gamma = 0.2\)

References
دراسات طيفية لمعقدات النيكل (II) والكروم (III) مع بعض الحوامض العضوية في المحاليل المائية

بحيى عبد المجيد العبدي
قسم الكيمياء- كلية العلوم للبنات- جامعة بغداد

الخلاصة

تم في هذا البحث تحضير معقدات النيكل (II) والكروم (III) مع الجذور الحاضمية العضوية التالية: 8- كولتولينات، الفثالات، الكلاسينينات، الانترابولات، السلافيلات، اهباريات وتورات، وقد سجلت لطيفات الاصدار الإلكترونية لها في المنطقة المرنية والفقه البنفسجية، وقد حسبت المعاملات النغليوكرتيزية (β) لها وتبين ان مقدار التأثير التساهمي بين الأيونات السالبة والمرمية يتغير كثيرا بسبب تأثير البول الذي تحدثه الكترونات مستوى 6g عند أيونات الكروم (III)، كذلك امكن ترتيب الليكانيات حسب زيادة قابلية تأصرها التساهمي وكم ألي: 8- كلاسينينات > فثالات > كولتولينات > اهباريات = سلافيلات = ماء.
بناءً على حساب معاملات المجال الليكانيدي لجوركيس (P_b) وتبين أنها تعتمد مع النمط التالي: 8- سلافيلات > كلاسينينات > فثالات > اهباريات > ماء > كولتولينات.