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, anthranillate, 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 (β) was calculated. Results showed that covalency between metal ions and ligands is largely affected by π - bonding due to t_{2g} electrons, the ligands could be arranged according to their increased tendency for covalent bonding (h_{lig}) as follows:

H_2O < sulph <phth <Anth<8-quino<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-quino<H_2O <Anth<Hipp <Phth<gly<sulph

Introduction

In the free atom or ion, measures of the energy seperations of the various Russell- saunders states are the Racah parameters (B) and (C).

In complexes, measures of the energy separation of sates of the same spin multiplcity have energy differences multiples of $(\overline{B})$, and for states of different multiplicity are expressed as sums of multiples of both $(\overline{B})$ and $(\overline{C})$[1]. $(\overline{B})$ is less than (B) of the free ion and $(\overline{C})$ 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 comlexing is taking place where electron delecalization 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[2]. 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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$F^- < H_2O < NH_3 <$ Oxalate ~ en < - NCS^- $< Cl^- \sim CN^- < Br^- < I^-$.

The positions of the varoius metal ions according to their covalent tendencies with respect to bond formation as expected from the view point of " polarization" forces causing larg distortion of the ligand's electronic structures are approximately[3].

Mn(II)<Ni(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[4] sine 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 [$Co(NH_3)_5NO_2]^{+2}$ 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 nepholauxetic 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 raizaed to 60°C and maintained for period of one hour, then the solutions were cooled in an ice bath, the metal complex crystals were seperated, dried in a desiccator, analysied for metal ions, ligands and water of hydration in the usual procedures[5].

Apparatus

Schemtzo (U.V- vis) recording spectrophotometer equiped with quartiz cells were used in all measurments.

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[6] :

$\nu_1 = 10\,Dq$ $\quad \nu_2 = 18\,Dq - X$ $\quad \nu_3 = 12\,Dq + 15\,B + X$

the ratio $(\overline{B}/B)$ which is known as the nephelauxetic ration (β) is useful in determining the nephelauxetic parameter (K_M) of the metal ion and the nephelauxitic parameter (h_x) of the ligand according to the equation:

$$(1-\beta) = K_M \cdot h_X \,\ldots\ldots\ldots\ldots(1)$$

B values are known for many metal ions in the free state. They are 918 cm^{-1} for Cr^{+++} and 1030 cm^{-1} for Ni^{++}. $(\overline{B})$ values of the complexes could be calculated from the energy level diagrams of the metal ions under different symmetries. For the d^3 and d^8 systems under investigation, the energy level diagram is represented by figure (3) for both ions.

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

$$10Dq = g_{ion} \cdot f_{lig} \,\ldots\ldots\ldots(2)$$

where g_{ion} and f_{lig} are the field factors of the metal ions and the ligands respectively. Values of these factors for the varoius 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 sulphanilated ions represent strong field case.

Discussion

Electronic spectra of chromium (III) complexes

Chromium (III) is the stablest oxidation state of the element [7] where the energy level (t_{2g}) being half filled, octahedral complexes are the most commen in chromium (III) compounds, the electroic transitions in the aquo complexes are (3):

$$\bar{\nu}_1 \quad \left[A_{2g} \rightarrow T_{2g}(F), 17.400 cm^{-1}\right]$$

$$\bar{\nu}_2 \quad \left[A_{2g} \rightarrow T_{1g}(F), 24.700 cm^{-1}\right]$$

$$\bar{\nu}_3 \quad \left[A_{2g} \rightarrow T_{1g}(P), 37.000 cm^{-1}\right]$$

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 planner one. On the other hand, the characeristic absorptions in tetrahedral complexes are three bands related to the transitions(3):

$${}^3T_1(F) \rightarrow {}^3T_2(F)$$
$${}^3T_1(F) \rightarrow {}^3A_2(F)$$
$${}^3T_1(F) \rightarrow {}^3T_1(P)$$

since the crystal field splitting (Dq_t) in tetrahedral symmetry is 4/9 (Dq_o) of that of octahedral one,therefore asborptions 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 ${}^3T_1(P) \leftarrow {}^3T_1(F)$

and a weak band at either side of the latter band representing the spin forbiden transitions, also it shows abserption band at 7.000 cm^{-1} related to transitions

${}^3A_2 \leftarrow {}^3T_1(F)$, the third band which represents the trnsitions ${}^3T_1(F) \leftarrow {}^3T_1(P)$ 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 $3d^8$ configuration will suffer splitting as can be seen in fig(4) the expected three transitions are(3):

$$\bar{\nu}_1 \quad \left[{}^3A_{2g} \rightarrow {}^3T_{2g}(F)\right] 7,000-13,000 cm^{-1}$$

$$\bar{\nu}_2 \quad \left[{}^3A_{2g} \rightarrow {}^3T_{1g}(F)\right] 11,000-28,000 cm^{-1}$$

$$\bar{\nu}_3 \quad \left[{}^3A_{2g} \rightarrow {}^3T_{1g}(P)\right] 19,000-28,000 cm^{-1}$$

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 Ni^{++} ion) also we have a metal ion possesses (t_{2g}) electrons only (case of Cr^{+++} ion).in general low (β) values obtained for Cr^{+++} complexes is an indication of extensive delocalization of (d) electrons[7], while high (β) values for Ni^{++} complexes is a consequance 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 . sulphanilate, glycinate, 8-quinolinate, anthranillate and hippurate. From the values of $h_{(lig)}$ the nephelauxitic 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-quine< Hipp<gly.

The magnitued 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_{ion}) and the nature of the ligand(f_{lig}), from the results of tabe(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_{lig}) as a measure for this tendency as follows:

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

finallly, the quantitative study of electron delocalization is only just begining[2], 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

Wave No.	Ligands KHP	8-hydroxy quinoline	Anthranillic Acid	Sulphanillic Acid	Gly	Hippuric Acid
$\bar\nu_1$	9433.9	10235.4	10235.4	10233.5	10277.5	10224.9
$\bar\nu_2$	10101.0	12722.6	11389.5	11682.5	11750.8	13286.2
$\bar\nu_3$	17857.1		27100.2	13368.9		

Table (II)

Assignments of absorption bands and Nephelauxitic parameters

Complexes 0.02M	$\bar\nu_1 cm^{-1}$	$\bar\nu_2 cm^{-1}$	$\bar\nu_3 cm^{-1}$	B'	β'	h_{lig}**	h_{av}
$Cr(H_2O)_6^{+3}$	17271.1	23980.8	38793.9	730.7	0.796	1.02	1.01
$Ni(H_2O)^{+2}$	8615.7	13586.9	25445.3	879	0.853	1.01	
$Cr(phth)_3^{-3}$	19140.	23963.3	40066.3	440.6	0.48	2.60	2.65
$Ni(phth)_3^{-4}$	10229.7	15950.8	25168.0	696	0.676	2.70	
$Cr(quin)_3$	15475.0	19808.0	32675.8	404	0.440	2.80	2.85
$Ni(quin)_3^{-1}$	7830.0	12684.0	20878.4	671	0.652	2.90	
$Cr(sulp)_3$	20184.0	2579.1	42466.8	514	0.56	2.20	2.25
$Ni(sulp)_3^{-1}$	10277.4	13404.8	28612	746	0.724	2.30	
$Cr(anth)_3$	17953.0	27932.9	32051.0	480	0.444	2.77	2.74
$Ni(anth)_3^{-1}$	10255.0	13550.1	27624.3	694	0.673	2.71	
$Cr(gly)_3$	18552.8	24937.6	33333.3	174	0.189	4.05	3.91
$Ni(gly)_3^{-1}$	10224.9	13550.1	25575.5	563	0.546	3.78	
$Cr(hip)_3$	17361.1	21614.4	36252.0	385	0.42	2.9	2.95
$Ni(hip)_3^{-1}$	10214.5	15729.5	24800.0	659	0.64	3.00	

$\beta' = B'/B$ where B_{Ni}^{+2}=1030 cm^{-1} and B_{Cr}^{+3}=918 cm^{-1}

**$(1-\beta) = h_{lig} \times K_M$, where K_{Ni}^{+2} = 0.12 and K_{Cr}^{+3} =0.2

Tabel (III)

crystal field splitting (10Dq) and Jorgensen's field factor of the ligand (f_{lig})

Complex	10 Dq $\bar\nu cm^{-1}$	10 Dq KJ/mole	$f_{(lig)}$	Average $f_{(lig)}$
$Cr(H_2O)_6^{+3}$	17271.1	206.4	0.992	0.991
$Ni(H_2O)_6^{+2}$	8615.7	102.9	0.990	
$Cr(phth)_3^{-3}$	19140.0	228.7	1.100	1.138
$Ni(phth)_3^{-4}$	10224.9	122.2	1.175	
$Cr(quin)_3$	15475.0	184.9	0.889	0.895
$Ni(quin)_3^{-1}$	7830.0	93.6	0.900	
$Cr(sulp)_3$	20184.0	241.2	1.160	1.170
$Ni(sulp)_3^{-1}$	10277.4	122.8	1.180	
$Cr(Anth)_3$	17953.0	214.5	1.030	1.104
$Ni(Anth)_3^{-1}$	10255.0	122.5	1.178	
$Cr(gly)_3$	18552.8	221.7	1.060	1.168
$Ni(gly)_3^{-1}$	10224.9	122.2	1.175	
$Cr(Hipp)_3$	17361.1	207.5	0.990	1.092
$Ni(Hipp)_3^{-1}$	10214.5	122.0	1.174	

Notes: (1) all solutions where of 0.02 molar concentration in water

(2) Jorgensen's equation[9]: 10 Dq = f_{lig} X g_M , where g_{Ni}^{++} = 8700 cm^{-1} and g_{Cr}^{+++} = 17400 cm^{-1}

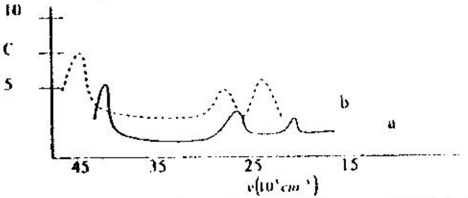


Fig (1) the spectrum of (a) $[Cr(H_2O)_6]^{+3}$, (b) $[Cr(sulphanilate)_3]$

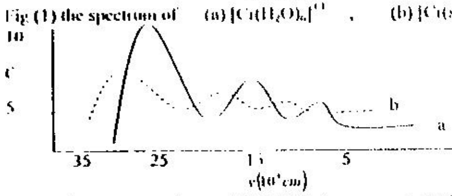


Fig (2) the spectrum of (a) $[Ni(H_2O)_6]$, (b) $[Ni(sulphanilate)_3]^{-1}$

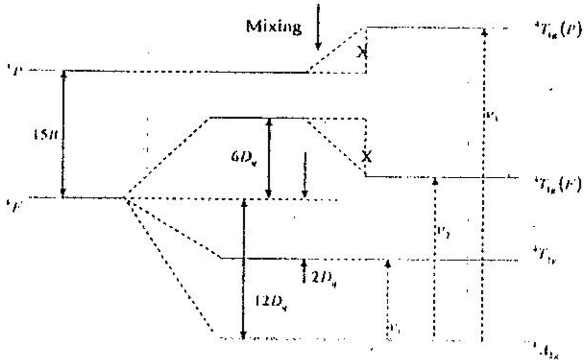
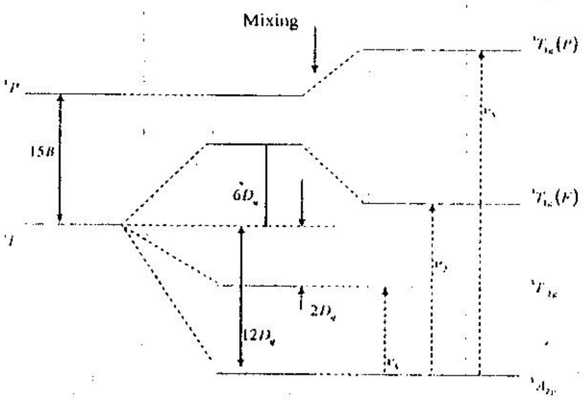


Figure (3): Splitting of ^4F and ^4P terms of a $3d^3$ ion in octahedral fields.



Figure(4) : Splitting of ^3F and ^3P terms of $3d^8$ ion in octahedral fields.

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

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الخلاصة

تم في هذا البحث تحضير معقدات النيكل (II) والكروم (III) مع الجذور الحامضية العضوية التالية ٨- كوينولينات ، الفثالات ، الكلايسينات ، الانثرانيلات ، السلفانيلات والهبيورات ، وقد سجلت اطياف الامتصاص الالكترونية لها في المنطقة المرئية والفوق البنفسجية ، وقد حسبت المعاملات النفيلوكزيتية (β) لها وتبين ان مقدار التأصر التساهمي بين الايونات السالبة والموجبة يتاثر كثيرا بسبب تأصر باي الذي تحدثه الكترونات مستوى t_{2g} عند ايونات الكروم (III) ، كذلك امكن ترتيب الليكاندات حسب زيادة قابلية تاصرها التساهمي وكما يلي: -

كلايسينات > هيبورات > ٨—كوينولينات > انثراينلات > فثلات > سلفانيلات > ماء .

كذلك حسبت معاملات المجال الليكاندي لجوركنسن (F_{lig}) وتبين انها تتماشى مع النمط التالي :-

سلفانيلات > كلايسينات > فثالات > انثرانيلات > ماء > ٨- كوينولينات.