

Comparative Crystal Field Studies of Some Ligand of Cr³⁺ Complexes

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Received: June 4, 2017

Accepted: August 19, 2017

Online Published: September 1, 2017

doi: 10.23918/eajse.v3i1sip109

Abstract: Chromium (III) complexes of nominate ligands are well recognized for their biological significance along with their anti-carcinogenic, anti-bacterial, and anti-fungal properties. In this investigation a range of Cr³⁺ complexes with diverse ligands were examined; and categorized with ultra-violet-visible, UV-Vis, spectrometer. Crystal field theory is an electrostatic method, utilized to characterize the fragmentation in *d*-orbital metal energies. It offers an expected explanation of the electronic energy levels that control the UV-Vis spectra. Accordingly, complexes' crystal field splitting parameters (Δ_o) are measured through the transition-band using the maximum wavelength. Similarly an additional method, comprising Tanabe-Sugano (TS) diagrams, has been utilized to compute crystal field splitting parameters for assessment. Thus, good agreement was found between both techniques. The configuration of the ligands in increasing order is found to be (H₂O) Cl < urea < H₂O < OX < NCS < OX H₂O < *acac* < *en* Cl < NH₃ NCS < *en* which coordinate mostly with the spectro-chemical series. Therefore (H₂O) Cl is the weakest ligand, while ethylenediamine (*en*) is the strongest one among the investigated ligands of Cr³⁺ complexes. Clearly strong ligands such as; ethylenediamine is considerably influences the coordination geometry of the metal complexes which effect on the deposit morphology and other physical and chemical properties.

Keywords: Crystal Field Theory, Ligand, Cr³⁺, UV-Visible Spectrum, Tanabe-Sugano Diagrams

1. Introduction

A complex is an amalgamation of a dominant metal-ion bounded by neutral molecules or ions representing a ligand (Burger, Belcher, & Freiser, 2013). Transition metal complexes are normally colored. These colors are recognized to be caused from the energy change between the separated *d*-shells. The quantity of separation of *d*-shells, on one hand reliant upon; the size, oxidation number, complex geometry and nature of metal ion and on the other hand it depends on the nature and geometry of the ligand. Therefore, amalgamations of metal ions and ligands produce metal complexes. The *d*-block metals ions possess low energy unoccupied *d*- and *p*-orbitals. These type of orbitals might take a single pair of electrons from certain species, recognized as ligands, to generate a co-ordinate bond between the ligand and the metal ion (Neuss, 2001). Thus, three orbitals are at low energy and two orbitals are at high energy as a result of octahedral ligands. The variance in energy of these orbitals characterize a frequency of light ($\Delta E=hf$), emphasizing that *E* is energy, *h* is Planck's constant and *f* is the frequency, which is in the visible region of electromagnetic spectrum. The energy difference, between the upper (*e_g*) and lower (*t_{2g}*) energy levels, known as; Octahedral Crystal Field Splitting Parameter (Δ_o) or, $10 D_q$.

The usage of a Tanabe-Sugano (TS) diagram in spectral investigation is reasonably simple. Figure 1 shows a basic Tanabe-Sugano diagram for a *d³* metal ion. Transitions between the ⁴A_{2g} ground state and excited states, possessing the similar multiplicity, can be characterized as perpendicular lines

among the horizontal axis and the lines signifying the excited states.

The TS diagrams (Tanabe & Sugano, 1954b) are very suitable for the expectation of electronic states not only of the two probable ground states but also of higher excited states beneath the impact of an octahedral ligand field. In Figure 1 the TS diagram for the d^3 arrangement are presented. It demonstrates electronic states and the energies of excited states in the Racah parameter units (Racah, 1942) of electron-electron repulsion B corresponding to the relevant ground state, against the ligand field power in $10D_q$, equally in units of B .

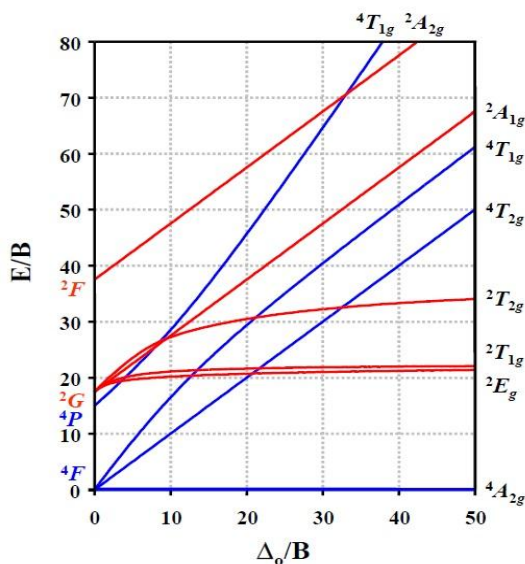


Figure 1: Tanabe-Sugano diagram for transition metals of d^3 configuration. Energy of the excited electronic states, relative to ground state, versus ligand field strength in units of Racah parameter B

Tanabe and Sugano (Tanabe & Sugano, 1954a, 1954b) calculated the energy levels for $3d^N$ ions in an octahedral field and schemed these as diagrams (Figure 1). These calculations can also be utilized for ions in tetrahedral fields, only that the diagram for a $3d^{10-N}$ ion has to be utilized. In addition, the crystal field strength is reduced from its octahedral value. For instance, a $3d^3$ ion in tetrahedral symmetry has an identical diagram as a $3d^7$ ion in octahedral symmetry with the reduced value of D_q . The parameters D_q , B and C are typically determined by fitting experimental data.

The status of splitting parameter of the d -orbitals and consequently the amount of Δ_o , reliant upon numerous parameters, comprising the charge on the metal, the size of the metal, and the nature of the ligand.

This investigation focuses only on the influence of nature of ligand, since there are a lot of d -block metals and it is not easy to study the nature of the metal in parallel with controlling the metal charge. Chromium (Cr), which is in the first row of transition metals, exhibits more than common oxidation state (Sharpe, 1976). Correspondingly, this investigation examines the chromium metal, since Chromium compounds, specifically Cr^{+3} compounds, are d^3 and their electronic spectral features are sensibly understandable.

2. Experimental Procedures

UV-Visible spectroscopy is very convenient as an analytical technique in chemical and biochemical research for two reasons: to classify some functional groups in the molecules and to measure concentration of a material in solution (Pavia, Lampman, Kriz, & Vyvyan, 2008). UV-Vis spectroscopy is work upon the absorption of light through the sample, such that electronic transitions will be produced. The energy that a molecule owns can be assigned definite energy levels, or states. In UV-Vis spectroscopy, a photon beam is passed through a sample, and absorption causes excitation of electrons in the discrete states of the molecules in the sample. These excitations can cause

transitions between the energy levels.

A Shimadzu Model UV-1601 Spectrophotometer was carried out to compute the solvatochromic shift of the nominated solution compositions in the visible absorbance spectrum. The package UV PROBE was utilized to achieve the λ_{max} values of the UV-Vis region of all Cr samples. Neat samples of Cr complexes were analyzed by adding same amount of deionized water for all compounds to confirm a clear signal of the absorption peaks. The reference cell was filled with deionized water. The spectrums of the solvatochromic probe in the arrangements were computed at a precision of 0.05nm/ data-point. Therefore, the predicted unconfident in the wavelength maximum is smaller than 0.5 nm. The cells were synthetic quartz glass with a path length of 10 mm and the baseline was obtained with the empty cells in place. Measurements were taken between 1100 and 220 nm at 0.1 nm intervals. Spectra were measured from 1100 nm to 220 nm, at ambient temperature.

3. Theory

The ligand field splitting parameter differs methodically with the characteristics of the ligand, as shown in Figure 2. The spectro-chemical series organizes ligands in order of increasing energy of $e_g \rightarrow t_{2g}$ transitions that take place once they are obtainable in a compound, and are available below a selection of ligands. Ligands producing a weaker ligand field are to the left in the series and ligands generating a substantial ligand field are lying at the right end (Bersuker, 2010).

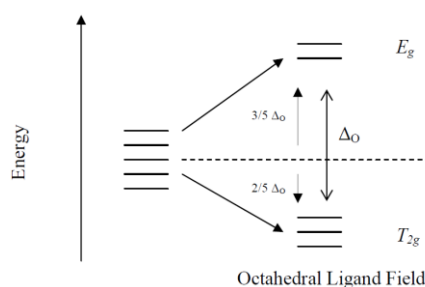


Figure 2: The separation of the orbitals into two sets is called a ligand-field splitting parameter.

The splitting pattern relies upon a complex interrelationship between numerous parameters. Nature of a contamination ion, its nearby environments and equilibrium features of the surroundings are amongst these parameters. In the $3d$ ions open electron shell situation the splitting is quantitatively characterized by the so-called cubic crystal field strength $10D_q$. $10D_q$ is well-defined as the energy separation between the anti-bonding e_g and t_{2g} orbitals of the principal ion (Sugano, Tanabe, & Kamimura, 1970). e_g and t_{2g} identify the equilibrium properties of the wave functions of the split states converting in agreement with consistent complicated representations of the octahedral, O_h , group. In crystal field theory, a ligand single pair is molded as a negative point charge that keeps away electrons in the d orbitals of the dominant metal ion. The theory focuses on the causing splitting of the d orbitals into groups with diverse energies, and utilizes that splitting to justify and associate the optical spectra, thermodynamic equilibrium, and magnetic properties of complexes (Newman & Ng, 2007).

In the existence of an octahedral crystal field, d orbitals are divided into a lower energy triply degenerate set (t_{2g}) and a upper energy doubly degenerate set (e_g) alienated by an energy Δ_o ; the ligand field splitting factor increases together with a spectro-chemical chain of ligands and differs with the individuality and charge of the metal atom (Atkins, 2010). Electronic characteristics of a complex are confidentially connected to its central metal ion. Therefore, it is not commonly desirable for the state even if a certain ligand provides a large or small ligand field splitting parameter without the metal ion consideration. As a general rule Δ increases with increasing oxidation number and has an increasing tendency as you go down to the group (Bersuker, 2010).

Precise explanations for the excited sate energy levels in terms of Δ_o , B and C are found from TS matrices. Although, these are very dense (10×10) matrices and hand computation are not practicable.

Therefore Tanabe-Sugano have designed energy level illustrations recognized as TS diagrams or energy level diagrams. The TS diagrams are effective as long as the value of B , C and Δ_o are smaller for a compound than for the free ion value. Assessable clarification of electronic absorption spectra is conceivable by means of TS diagrams. These illustrations are extensively used to link and understand the ions spectra of all kinds, from d_2 to d_8 . TS diagrams are suitable equally for high spin and low spin complexes. The x -axis in TS diagrams signifies the ground state expression. Moreover, in TS illustrations, the axes are alienated by B , the inter-electronic repulsion factor. The x -axis signifies the crystal field power in terms of Δ_o/B or Δ/B and the y -axis signifies the energy in terms of E/B . The energies of the numerous electronic states are assumed in the TS illustrations on the vertical axis and the ligand field strength rises from leftward to rightward on the horizontal axis. The signs in the diagram neglect the subscript, g , accepting that all states are grade states. Similarly, in TS illustrations, the zero of energy for any specific d_n ion is occupied and represent the ground state energy. Irrespective of the ligand field power, at that time, the horizontal axis signifies the energy of the ground state since the vertical axis possesses the E/B units and x -axis is also possesses the Δ/B units. Therefore, the unit of energy in TS diagram is B , Reach Parameter. The values of B are dissimilar for dissimilar ions of the same d_n (otherwise unlike d_n alignment) which is presented in the highest of each diagram. One TS diagram is utilized for entire members of an isoelectronic collection. Likewise some hypothesis is stated about the equivalent value of C/B (Reddy, Reddy, & Endo, 2012).

4. Results and Discussion

In order to evaluate Δ_o in this investigation, two analytical methods were utilized. The first method is easy and straightforward procedure, which includes simply the computation of Δ_o by means of the highest wavelength band from the UV-Vis spectrum. This process permits us to build a classification between the utilized ligands (Öztürk, Zümreoglu-Karan, & Can, 2008). Nevertheless, this method does not produce precise datas. Accordingly, the band energy with highest wavelength is expected to possess the energy of Δ_o and the further relations between d -electrons are ignored.

Figure 3 displays all spectra of Cr^{+3} complexes utilized in the investigation. The maxima and minima values of wavelengths can be summarized in Table 1. It can be noted from Figure 4 and Table 1 that, the highest λ_{max} can be seen in $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]$ which is 635 nm. Correspondingly, the highest λ_{min} is belong to $[\text{Cr}(\text{urea})_6]\text{Cl}_3$. Whereas the lowest λ_{max} and similarly lowest λ_{min} is recorded for $[\text{Cr}(\text{en})_3]\text{Cl}_3$. This might be due to the chemical composition of acetylacetone. On the other hand, apart for $[\text{Cr}(\text{acac})_3]$ the absorption values at maxima in all complexes are relatively similar. As *acac* has resonance structure, might be the reason of the alteration. Moreover, as the external part of the complex is organic, and the complex is hydrophobic, which may affect the spectra.

Since, the maximum wavelength has the energy Δ_o , thus:

$$\Delta_o = E = \frac{hc}{\lambda_{\text{max}}} \quad (1)$$

where E is the energy, h is the Planck constant, c is the speed of light and λ_{max} is the maximum wavelength which can be obtained from the UV-Vis spectrum. The second method to evaluate Δ_o is the Tanabe-Sugano diagram (Figure 1), which assistances us to compute numerous factors of a complex precisely. The TS diagrams contain the electronic collaborations between the d -electrons; therefore the intentions utilizing this diagram are further truthful. Nevertheless, as there are simply 2 more electrons in a d_3 complex, the collaborations are negligible, but there is tiny alteration between the standards intended by the first technique and the second technique. Thus, to utilize the Tanabe Sugano diagram, the wavelengths should be converted to wavenumbers. Through judging the resultant heights (E/B) of the symmetry states at definite values of Δ_o/B , the Racah parameter can be found by computing B parameter. However, B is originating from the E/B ratio where E is the minimum transition energy in cm^{-1} . Δ_o can be calculated from the Δ_o/B ratio straightforwardly once B is calculated (Weller, Overton, Rourke, & Armstrong, 2014). After calculating Δ_o from UV-Vis

spectra and Tanabe-Sugano diagram the evaluated data recorded in Table 2. It is shown that there are negligible differences in Δ_o measured with the highest wavelength band and Δ_o calculated with using TS diagrams.

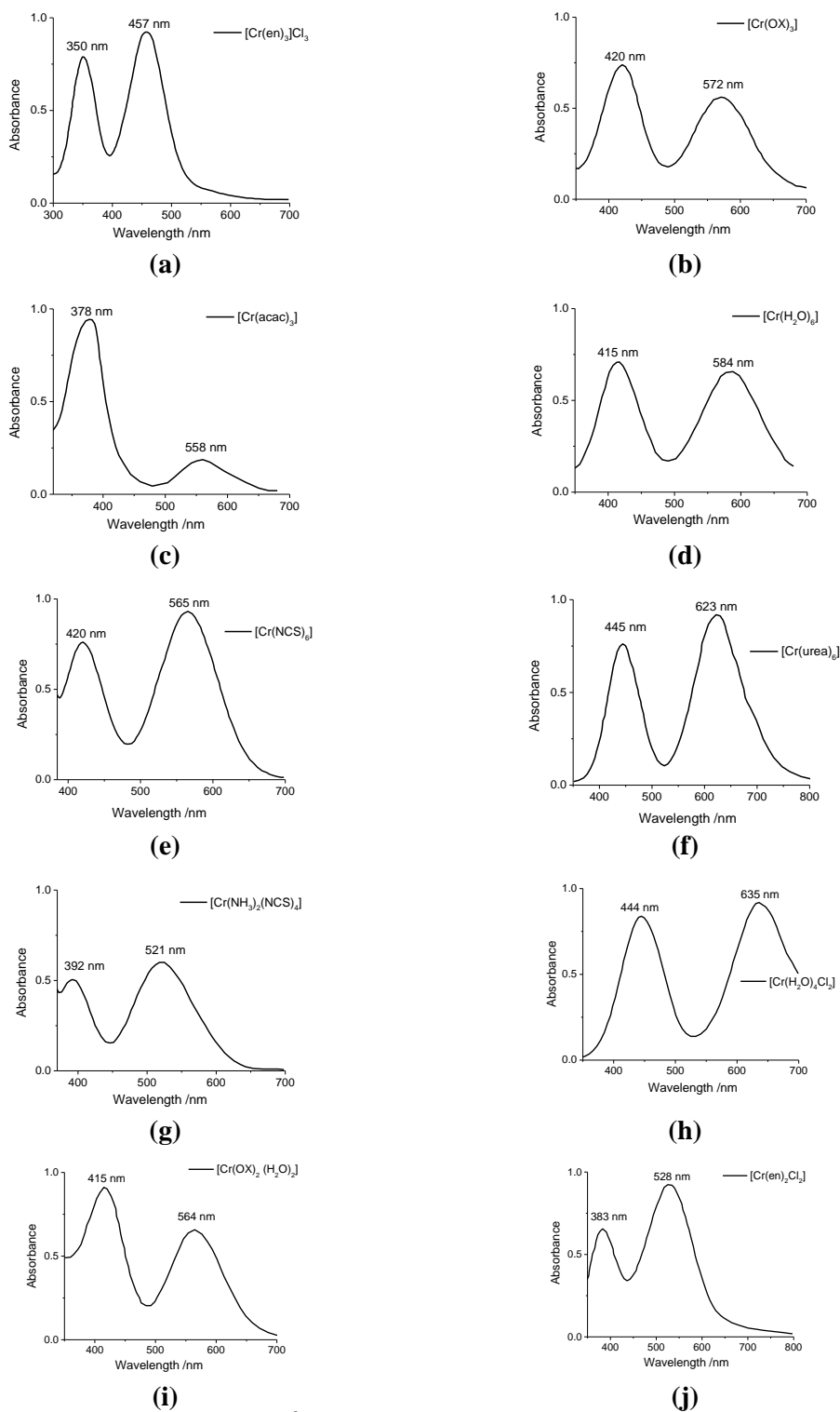


Figure 3: UV-vis spectra of Cr^{+3} complexes used in the experiment; **(a)** $[\text{Cr}(\text{en})_3]\text{Cl}_3$, **(b)** $[\text{Cr}(\text{OX})_3]$, **(c)** $[\text{Cr}(\text{acac})_3]$, **(d)** $[\text{Cr}(\text{H}_2\text{O})_6]$, **(e)** $[\text{Cr}(\text{NCS})_6]$, **(f)** $[\text{Cr}(\text{urea})_6]\text{Cl}_3$, **(g)** $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$, **(h)** $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]$, **(i)** $[\text{Cr}(\text{OX})_2(\text{H}_2\text{O})_2]$ and **(j)** $[\text{Cr}(\text{en})_2\text{Cl}_2]$.

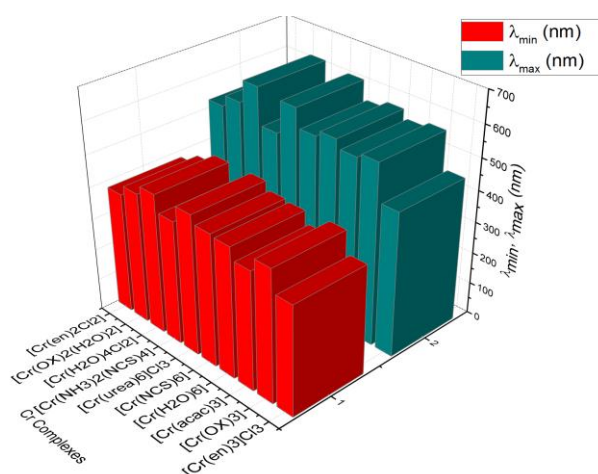


Figure 4: The maxima and minima values of wavelengths of Cr⁺³ complexes

Consequently, strong-field ligands can cause a large splitting (Δ_o) of the d-orbitals. In the investigated complexes, Δ_o is greater than the pairing energy and electrons are dynamically favored to completely fill the low energy orbitals before occupying higher energy orbitals (Van den Heuvel, Hendrickx, & Ceulemans, 2007).

Table 1: The maxima and minima values of wavelengths of Cr⁺³ complexes

Cr complexes	λ_{\min} (nm) ± 1	λ_{\max} (nm) ± 1
[Cr(en) ₃]Cl ₃	350	457
[Cr(OX) ₃]	420	572
[Cr(acac) ₃]	378	558
[Cr(H ₂ O) ₆]	415	584
[Cr(NCS) ₆]	420	565
[Cr(urea) ₆]Cl ₃	445	623
[Cr(NH ₃) ₂ (NCS) ₄]	392	521
[Cr(H ₂ O) ₄ Cl ₂]	444	635
[Cr(OX) ₂ (H ₂ O) ₂]	415	564
[Cr(en) ₂ Cl ₂]	383	528

Table 2: Δ_o calculated with the longest wavelength band and Δ_o calculated with using Tanabe-Sugano diagrams and the percentage difference between the two utilized methods

Cr complexes	Δ_o (J/mole) ± 1 Tanabe-Sugano	Δ_o (J/mole) ± 1 UV-vis	$\Delta(\Delta_o)$ (J/mole) ± 1	Percentage difference (%)
[Cr(en) ₃]Cl ₃	261612	261268	344	0.13
[Cr(OX) ₃]	209014	208894	120	0.057
[Cr(acac) ₃]	214263	213710	553	0.25
[Cr(H ₂ O) ₆]	204720	204680	40	0.019
[Cr(NCS) ₆]	211605	211302	303	0.14
[Cr(urea) ₆]Cl ₃	192038	191900	138	0.071
[Cr(NH ₃) ₂ (NCS) ₄]	229499	229362	137	0.059
[Cr(H ₂ O) ₄ Cl ₂]	188426	188279	147	0.078
[Cr(OX) ₂ (H ₂ O) ₂]	211979	210700	1279	0.60
[Cr(en) ₂ Cl ₂]	226432	226352	80	0.035

Several limitations have reduced the strength of assumption. To start with, as soon as the ligand is changed, lots of parameters such as field and molecular dimensions also changes, therefore it is not definite that which parameter of ligand control the Δ_o of the complex. It can be noticed that, strong field ligands possess greater Δ_o than weak field ligands, nevertheless it appears to be independent from molecular mass of ligands and the denticity (*i.e.* the donor groups' number from that ligand joined to the corresponding central atom).

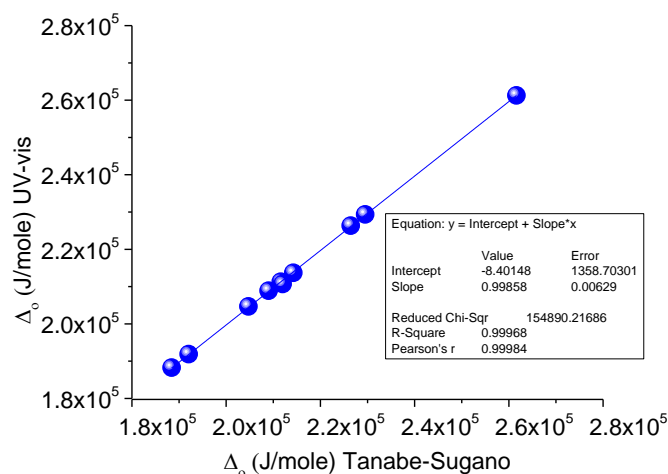


Figure 5: Δ_o measured from UV-vis spectra and Tanabe-Sugano diagram

It can be notice from Figure 5 that there are good agreement between Δ_o measured from UV-Vis spectra and Tanabe-Sugano diagram. In addition, the ranking of the ligands in increasing order is found to be (H₂O) Cl < urea < H₂O < OX < NCS < OX H₂O < *acac* < *en* Cl < NH₃ NCS < *en* which come to an agreement with the spectro-chemical series. Therefore (H₂O) Cl is the weakest ligand, while ethylenediamine (*en*) is the strongest one among the investigated ligands of Cr³⁺ complexes. This is, most likely because [Cr (*en*)₃]³⁺ complex possess mirror image arrangements specifically enantiomers of optical isomers. The ligand bonds through the single pairs of electrons on the nitrogen which are contributed to form the metal-ligand dative covalent bonds (Winter, 2015). It can be understood that, strong ligands such as; ethylenediamine is substantially effects the coordination geometry of the metal complexes which influence on the deposit morphology and other physical and chemical properties (Drickamer & Frank, 2013). According to the obtained results, the small uncharged ligand molecules like urea and water are similar in size therefore their Δ_o are very close to each other.

5. Conclusion

Crystal Field Theory is a useful model for simple interpretation of spectra and ligand properties of first-row transition metal complexes. Numerous restrictions have reduced the strength of assumptions. Initially, once the ligand is altered, numerous parameters such as field and molecular dimensions also changes, thus it is not convinced that which parameter of ligand influence the Δ_o of the compound. Through explanation, strong field ligands possess higher Δ_o than weak field ligands, nevertheless it appears to be independent from molecular mass of ligands and the denticity (namely, the donor groups' number from that ligand connected to the equivalent central atom). Good agreement between Δ_o measured from UV-vis spectra and Tanabe-Sugano diagram obtained. It has been found that (H₂O) Cl was the weakest ligand, while ethylenediamine (*en*) was the strongest one among the investigated ligands. On the whole, the order of Δ_o values in increasing order for the utilized ligand were (H₂O) Cl < urea < H₂O < OX < NCS < OX H₂O < *acac* < *en* Cl < NH₃ NCS <

en which agrees in high manner with the spectro-chemical series.

6. Acknowledgement

The author would like to express his acknowledgement to the Salahaddin University for supporting him with available tools. He also would like to thank Dr. Samir Mustafa Hamad at Research Centre, Soran University in Erbil, for his insightful ideas, suggestions, and time for serving in our discussions.

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