Crystal Field Splitting Energy (Δ_0) and Racah Parameters (B) of Some Metal-Saccharine and Metal-Saccharine-Ethylenediamine Complexes

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Abstract

 $[M(sac)_2(H_2O)_4].2H_2O$ [sac = saccharinato anion, M = Fe(II), Co(II), Ni(II), and Cu(II)], and $[M(sac)_2(en)_2].2H_2O$ [sac = saccharinato anion, en = ethylenediamine, M = Fe(II), Co(II), Ni(II) and Cu(II)] were prepared in an aqueous medium. The compounds are crystalline of different colors and are ambiently stable. By examining their physico-chemical properties and relevant literature, the metal(II) ions in both $[M(sac)_2(H_2O)_4].2H_2O$ and $[M(sac)_2(en)_2].2H_2O$ complexes are octahedrally coordinated. In the former by four neutral H_2O molecules and two monoanionic sac ligands while in later, the octahedral sites fulfilled by two neutral bidentate ethylenediamine molecules and two monoanionic sac ligands. Splitting of the crystal field (Δ_o) and Racah parameter (B) of two sets of complexes $[M(sac)_2(H_2O)_4].2H_2O$ and $[M(sac)_2(en)_2].2H_2O$ are estimated from their electronic spectra using Tanabe-Sugano diagram of Co(II) and Ni(II) complexes while Δ_o values of Fe(II) and Cu(II) derivatives are calculated directly from their absorption maxima. Our experimental results show that for the studied ligands and the divalent transition metal ions, the Δ_o values vary according to the following order: Cu(II) > Fe(II) > Co(II) > Ni(II).

Keywords: Saccharine, Electronic spectra, Tanabe-Sugano diagram, Crystal field splitting, Racah parameter.

I. Introduction

In crystal field theory, the only role of the ligands in transition metal complexes has been to produce the splitting of the d-orbitals. The bonding between the metal and the surrounding ligand molecules was presumed to be purely ionic in nature¹⁻². The crystal field theory modified to admit that there is some covalent bonding in addition to electrostatic interaction between the metal ion and its ligands is known as the ligand field theory. The effect of ligands in expanding the d electron clouds has been named the nephelauxetic effect. The magnitude of the nephelauxetic effect may be conveniently expressed as the Racah interelectronic repulsion parameter $(B)^3$. The complexes of transition metals are usually colored, and they are capable of absorbing radiant energy in the infrared, ultraviolet, as well as visible regions. Tanabe-Sugano (T-S) diagrams are used in coordination and transition metal chemistry to predict absorptions in the UV-visible electromagnetic spectrum of complex compounds⁴⁻⁵. A Tanabe-Sugano diagram's x-axis is scaled by the B Racah Parameter and is expressed in terms of the crystal field splitting parameter, 10Dq, or Δ_a . The y-axis is scaled by B and expressed in terms of the energy of an electronic transition, E. While adjusting the strength of the octahedral ligand field, each line represents the energy of an electronic state. By using the E/B values (y-axis) and Δ /B (x-axis) to solve for B, the ligand field splitting energy, 10Dq is obtained⁶. Regarding the two sets of complexes [M(sac)₂(H₂O)₄].2H₂O and $[M(sac)_{\alpha}(en)_{\alpha}].2H_{\alpha}O$, crystal field splitting (Δ) and the Racah parameter (B) are estimated from their electronic spectra using Tanabe-Sugano (T-S) diagram of Co(II) and Ni(II) complexes while Δ values of Fe(II) and Cu(II) derivatives are calculated directly from their absorption maxima.

II. Experimental

Materials

Sodium saccharinate hydrate (C₇H₄NO₃S)Na.2/3H₂O, (NH₄)₂Fe(SO₄).6H₂O, CoCl₂.2H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, conc. H₂SO₄, and ethylenediamine were of reagent grade. Deionized water was used for making solutions.

Methods and Equipments

The melting points of the complexes were recorded in a Stuart Melting Point Apparatus, Model SMP 11, VWR International Ltd. UK with a capacity of recording the temperature up to 250°C. FTIR spectra were recorded between 4000-400 cm⁻¹ by a conventional KBr pellet method on a Perkin-Elmer FTIR spectrometer, 1760X. Each Pellet was prepared by mixing the sample with an appropriate amount of KBr using an absorbance spectroscopy accessory. The UV/Vis spectra were recorded using Ultraviolet and visible Recording Spectrometer, in the wavelength range, 200-1100 nm using ethanol as solvent. Magnetic susceptibility measurements were done using a Sherwood Scientific magnetic moment balance, Cambridge, England, Model Magway MSB Mk1.

Preparative procedure

The method of synthesis is simple and straight-forward. Since saccharin is insoluble in water, the reactions are carried out using water soluble Na-saccharin as the starting material in an aqueous medium.

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$\label{eq:total-distance} Tetra a quadis a ccharina to metal (II). dihydrate, \\ [M(sac)_2(H_2O)_4]. 2H_2O$

Saccharinato metal(II) complexes of the type $[M(sac)_2(H_2O)_4]$. $2H_2O$ [sac = saccharinato, M = Fe(II), Co(II), Ni(II), and Cu(II)] were prepared and isolated as described in the literature⁷⁻¹⁰.

$$(C_7H_4NO_3S)Na.2/3 \ H_2O \ + \ M(II) \ salt \ \stackrel{\textstyle H_2O}{\rightarrow} \\ [M(sac)_2(H_2O)_4].2H_2O$$

Bis(ethylenediamine)bis(saccharinato) metal(II). dihydrate, [M(sac)₂(en)₂].2H₂O

Saccharinato metal(II) complexes of the type $[M(sac)_2(en)_2]$. $2H_2O$ [sac = saccharinato, en = ethylenediamine, M =Fe(II), Co(II), Ni(II), and Cu(II)] were prepared and isolated as described in the literature¹¹⁻¹².

$$[M(sac)_2(H_2O)_4].2H_2O + 2en \xrightarrow{H_2O} [M(sac)_2(en)_2].2H_2O$$

Table 1. Data for the synthesis of [M(sac),(H,O),].2H,O.

(C ₇ H ₄ NO ₃ S)Na. 2/3H ₂ O, g	Metal(II) salts in water		Formula of the complexes	Yield, %	Color of the Complexes
0.4212	$(\mathrm{NH_4})_2\mathrm{Fe}(\mathrm{SO_4}).$ $6\mathrm{H_2O}$	0.3948 in 20 mL	[Fe(sac) ₂ (H ₂ O) ₄]. 2H ₂ O	94.8	Greenish yellow
0.4376	CoCl ₂ .2H ₂ O	0.2411 in 20 mL	[Co(sac) ₂ (H ₂ O) ₄].22H ₂ O	87.3	Shiny red
0.4771	NiCl ₂ .6H ₂ O	0.3734 in 20 mL	[Ni(sac) ₂ (H ₂ O) ₄].2H ₂ O	95.9	Green
0.4414	CuCl ₂ .2H ₂ O	0.1810 in 20 mL	[Cu(sac) ₂ (H ₂ O) ₄].2H ₂ O	90.0	Sky Blue

Table 2. Data for the synthesis of [M(sac)₂(en)₂].2H₂O.

$[M(sac)_2(H_2O)_4].2H_2O.$		Ethylana	Ethylene- Formula of the		G-1
Formula	Amount,	Ethylene- diamine, mL	complexes	Yield, %	Color of the complexes
[Fe(sac) ₂ (H ₂ O) ₄].2H ₂ O	0.5314 in 20 mL	0.1	[Fe(sac) ₂ (en) ₂].2H ₂ O	25.9	Dark Green
$[\mathrm{Co(sac)}_2(\mathrm{H_2O)}_4].2\mathrm{H_2O}$	0.5313 in 20 mL	0.1	$[\mathrm{Co(sac)}_2(\mathrm{en})_2].2\mathrm{H}_2\mathrm{O}$	44.6	Dark Red
$[\mathrm{Ni}(\mathrm{sac})_2(\mathrm{H}_2\mathrm{O})_4].2\mathrm{H}_2\mathrm{O}$	0.5311 in 20 mL	0.1	$[Ni(sac)_2(en)_2].2H_2O$	74.2	Purple
$[\mathrm{Cu(sac)}_2(\mathrm{H_2O)}_4].2\mathrm{H_2O}$	0.5324 in 20 mL	0.1	$[\mathrm{Cu(sac)}_2(\mathrm{en})_2].2\mathrm{H}_2\mathrm{O}$	22.7	Violet

III. Results and Discussion

Using previously published literature, complexes of saccharin-metal(II) and ethylenediamine-saccharin-metal(II) were prepared and characterized¹¹⁻¹². Some of the physicochemical characteristics of the complexes, including solubility, FTIR, UV-Visible spectrum investigations, and magnetic susceptibility, were evaluated and compared with the data from the literature in order to establish their structural geometries (Fig. 1).

Divalent transition metal complexes with octahedral shape exhibit electronic transitions in the visible range that are typically metal centered d→d transitions. These transitions are forbidden by the Laporte (orbital) selection rule, but they take place because the electronic wave functions are not entirely independent of the vibrational functions. The different electronic transitions of the complexes (Figs. 2-5) identified for the investigated metal(II) complexes are displayed in Table 3. They are relatively weak, and the T-S diagram is used for the interpretation of the electronic spectra of the complexes.

Fig. 1. Structural geometries of (a)[M(sac)₂(H₂O)₄].2H₂O and (b) [M(sac)₂(en)₂].2H₂O

Table 3. Electronic spectral data of studied complexes

Complexes	Wavelength, nm	Complexes	Wavelength, nm
[Fe(sac) ₂ (H ₂ O) ₄].2H ₂ O	947	$[Fe(sac)_2(en)_2].2H_2O$	651
$[Co(sac)_2(H_2O)_4].2H_2O$	507, 480	$[\mathrm{Co(sac)}_2(\mathrm{en})_2].2\mathrm{H}_2\mathrm{O}$	501, 369
$[Ni(sac)_2(H_2O)_4].2H_2O$	721,656,396	$[Ni(sac)_2(en)_2].2H_2O$	885, 543
$[Cu(sac)_{2}(H_{2}O)_{4}].2H_{2}O$	805	$[\mathrm{Cu(sac)}_2(\mathrm{en)}_2].2\mathrm{H}_2\mathrm{O}$	549

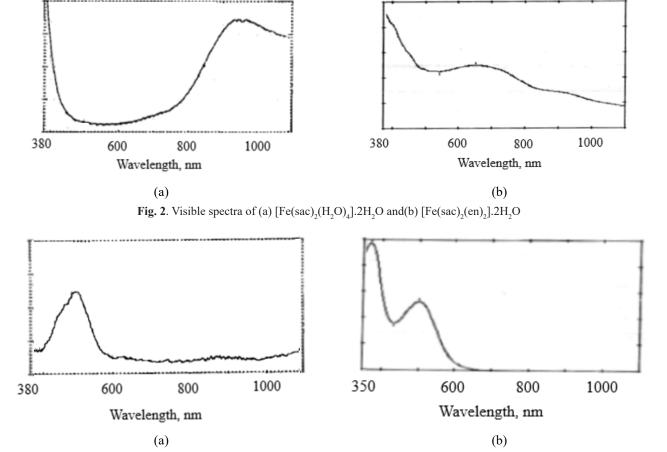
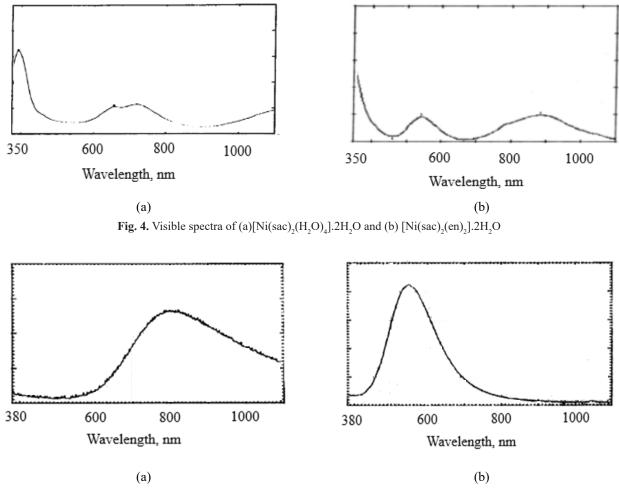


Fig. 3. Visible spectra of (a) $[Co(sac)_2(H_2O)_4].2H_2O$ and (b) $[Co(sac)_2(en)_2].2H_2O$



 $\textbf{Fig. 5.} \ \ \text{Visible spectra of (a)} \ \ [\text{Cu(sac)}_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O} \ \ \text{and (b)} \ \ [\text{Cu(sac)}_2(\text{en})_2].2\text{H}_2\text{O}$

Fe(II) (d⁶ ion) complexes: The strength of the ligand field has a important impact on the nature of the electronic spectrum. For a high spin octahedral Fe2+ ion, there is only one spin allowed transition $({}^5T_{2g} {\longrightarrow} {}^5E_g)$, which corresponds to one absorption band, however for low spin Fe²⁺ complexes, there are two spin allowed transitions $({}^{1}A_{lg} \rightarrow {}^{1}T_{lg}$ and ${}^{1}A_{lg} \rightarrow {}^{1}T_{2g})$ at relatively low energies. For the ligands such as $H_{2}O$, ethylenediamine and saccharinato anion used in this study are moderately strong, as indicated by their position in the spectrochemical series, their complexes with Fe(II) are high spin type because the formation of spin paired complexes requires a relatively strong field. Both [Fe(sac)₂(H₂O)₄].2H₂O and [Fe(sac)₂(en)₂].2H₂O are high spin complexes and exhibit a broad absorption band in their visible spectra (Fig.2) due to ${}^{5}\mathrm{T}_{2a} \rightarrow {}^{5}\mathrm{E}_{a}$, transition. The energies associated with the single spin-allowed transition are 10559.66 and 15360.98 cm⁻¹ for the compounds [Fe(sac)₂(H₂O)₄].2H₂O and [Fe(sac)₂(en)₅].2H₂O respectively. They are equal to their respective Δ_0 values. The T-S diagram cannot be used in these circumstances to derive the Racah parameters B¹³.

Co(II) (d' ion) complexes: The Co(II) in octahedral coordination has the ground state of ${}^{4}T_{10}$. The T-S diagram

exhibits that there are three excited states: ${}^4T_{2g}$, ${}^4A_{2g}$ and ${}^4T_{1g}$ (P). So, we can predict three spin allowed transitions. However, the absorption spectrum of high spin [Co(sac)₂(H₂O)₄].2H₂O complex does not show three spin-allowed bands. Instead, the spectrum shows a broad band. From the T-S diagram, the lowest energy transition is ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g}$ that is not found in the visible spectrum due to near IR energy of this transition. The main band is the energy transition ${}^{4}T_{1\sigma}(F) \rightarrow {}^{4}T_{1\sigma}(P)$ and the shoulder associated with the slightly higher energy transition ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$. Overlapping of peaks due to small energy difference makes broad band in the visible spectrum. [Co(sac)₂(H₂O)₄].2H₂O shows a broad band with a shoulder at 20,833.34 and 19,723.86 cm⁻¹ and [Co(sac)₂(en)₂].2H₂O shows two spin-allowed bands at 19,960.08, and 27,100.27 cm⁻¹ (Fig. 3) which are assigned in Table 3. The ratio of two energies for $[Co(sac)_3(H_2O)_4].2H_2O$ is given by $v_3/v_4 =$ 1.05. From the T-S diagram for the d⁷ system (Fig. 6), the following data can be figured out for high spin complexes. Now, by plotting v_2/v_1 vs. Δ/B (Fig. 7), we find that at v_2/v_1 = 1.05, the value of Δ /B = 12.0. The T-S diagram has Δ /B = 12, and the value of E/B for the lowest energy transition can be read out from E/B = 20. So we can write, 19,723.86 cm⁻¹ $^{1}/B = 20$. Therefore, Racah parameter, B = 19,723.86 cm⁻¹/20 = 986.19 cm⁻¹. Now Δ_o/B = 12, crystal field splitting energy, Δ_o = 11,833.80 cm⁻¹. The magnitude of Δ_o = 12,831.42 cm⁻¹ and B = 1,425.72 cm⁻¹ for [Co(sac)₂(en)₂].2H₂O is calculated by adopting the same procedure given above.

Ni(II) (d^8 ion) complexes: The spectrum of the d^8 complex [Ni(sac)₂(H₂O)].2H₂O shows two bands at 13,869.62 cm⁻¹ and 25,252.52 cm⁻¹ (Fig. 4), which are assigned as follows (Table 6). The ratio of these two energies is given by v_2/v_1 =

25,252.52/13,869.62 = 1.82. From the T-S diagram for the d^8 system (Fig. 8), the following data can be figured out (Table 7). Again, at $\Delta_o/B=8.25$, the value of E/B for the lowest energy transition can be read out from the T-S diagram as E/B = 17.04.So we can write, 13,869.62 cm⁻¹/B = 17.04. Therefore, B = 13,869.62 cm⁻¹/17.04 = 813.94 cm⁻¹. Now $\Delta_o/B=8.25$, therefore $\Delta_o=6715.005$ cm⁻¹.

Table 4. Absorption maxima and band assignment of Co(II) complexes

Complexes	$^{4}\text{T}_{1g} \rightarrow ^{4}\text{A}_{2g} (v_2),$ cm ⁻¹	${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)(v_{1}),$ cm^{-1}
$\boxed{ \left[\text{Co(sac)}_2(\text{H}_2\text{O})_4 \right].2\text{H}_2\text{O} }$	20,833.34	19,723.86
$[Co(sac)_2(en)_2].2H_2O$	27,100.27	19,960.08

Table 5. Derived data for the determination of Δ_0 and B for d⁷ ion

$\Delta_{\circ}/\mathrm{B}$	ν ₁ , cm ⁻¹	ν ₂ , cm ⁻¹	v_2/v_1
3.70	4.40	12.0	2.72
6.70	9.60	13.6	1.42
10.0	12.00	15.2	1.26
14.07	16.80	16.8	1.00

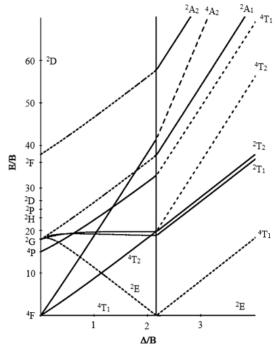


Fig. 6. Tanabe-Sugano diagram for d⁷ ion.

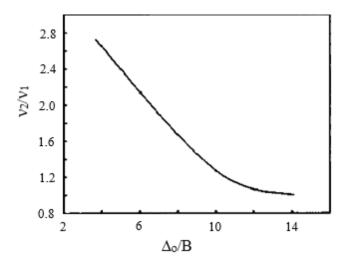


Fig. 7. A plot of v_2/v_1 vs. Δ_0/B for Co(II).

Complexes	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F) (v_{1})$ cm ⁻¹	$^{3}A_{2g} \rightarrow {^{3}T_{1g}}(P) (v_{2})$ cm ⁻¹
[Ni(sac) ₂ (H ₂ O) ₄].2H ₂ O	13,869.62	25,252.52
$[Ni(sac)_2(en)_2].2H_2O$	11,363.64	18,416.2

Table 7. Derived data for the determination of Δ_0 and B for d⁸ ion

Δ_{\circ}/B	v_1 , cm ⁻¹	v_2 , cm ⁻¹	v_2/v_1
10	16.30	28.15	1.73
15	23.33	35.56	1.57
20	28.89	45.92	1.59
25	34.81	54.07	1.56
30	40.00	62.22	1.55

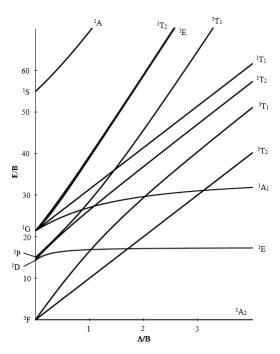
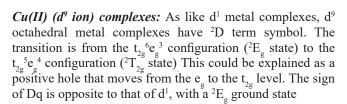


Fig. 8. Tanabe-Sugano diagram for d⁸ ion.



and a $^2T_{2g}$ excited state. The six coordinated Cu²⁺ complexes are mostly distorted from a regular octahedral geometry, with the axial ligands of the octahedral system further away from

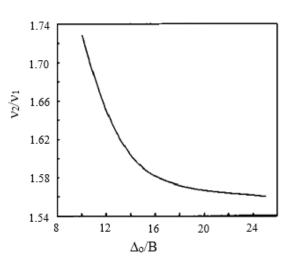


Fig. 9. A plot of v_2/v_1 vs. Δ_0/B for Ni(II).

the metal ion than the equatorial ligands due to Jahn-Teller distortion. The absorption spectra of Cu²+ complexes (Fig.5) broadened by distortion from octahedral symmetry may be further broadened by spin-orbit (L-S) coupling. The energies corresponding to the $^2{\rm E_g} \!\!\to\!\! ^2{\rm T_{2g}}$ transition are 12422.36 cm¹- and 18214.94cm¹- for the complexes [Cu(sac)_2(H_2O)_4].2H_2O and [Cu(sac)_2(en)_2].2H_2O respectively is equal to their respective Δ_o values. In such cases, the Racah parameters B cannot be determined using the T-S diagram. The $v_2/v_1, \Delta_o/B$, B, E/B, Δ_o of studied complexes are summarized in Table 8.

Complexes	v_2/v_1	Δ _o /B	B, cm ⁻¹	E/B	$\Delta_{\rm o}$, cm ⁻¹
[Fe(sac) ₂ (H ₂ O) ₄].2H ₂ O					10,559.66
$[Fe(sac)_2(en)_2].2H_2O$					15,360.98
$[Co(sac)_2(H_2O)_4].2H_2O$	1.05	12.00	986.15	20.00	11,833.80
$[\mathrm{Co(sac)}_2(\mathrm{en})_2].2\mathrm{H}_2\mathrm{O}$	1.35	9.00	1,425.72	14.00	12,831.42
$[Ni(sac)_2(H_2O)_4].2H_2O$	1.82	8.25	813.94	17.04	6,715.01
$[Ni(sac)_2(en)_2].2H_2O$	1.62	17.50	520.08	21.85	9,101.40
$[Cu(sac)_{2}(H_{2}O)_{4}].2H_{2}O$					12,422.36
$[Cu(sac)_2(en)_2].2H_2O$					18,214.94

Table 8. Derived data evaluated from Tanabe-Sugano diagram for d⁶, d⁷, d⁸, d⁹ ion

IV. Conclusion

 $[M(sac)_2(H_2O)_4].2H_2O$ and $[M(sac)_2(en)_2].2H_2O$ complexes were prepared in an aqueous medium. They were crystalline, different in color and stable at ambient condition. Crystal field splitting, Δ_a , and the Racah parameter (B) of two sets of compounds [M(sac)₂(H₂O)₄].2H₂O and [M(sac)₂(en)₂].2H₂O [M = Fe(II), Co(II), Ni(II)and Cu(II)] were calculated from their electronic spectra. The magnitude of $\Delta_{_{0}}$ and B were estimated from their d-d transitions using the Tanabe-Sugano (T-S) diagram for Co(II) and Ni(II) compounds, while the Δ values of Fe(II) and Cu(II) derivatives were calculated directly from their absorption maxima. Our experimental results demonstrate that irrespective of the ligands, the magnitudes of the crystal field splitting values, Δ_{o} , vary according to the following order: Cu(II) > Fe(II) > Co(II) > Ni(II). The Δ values of $[M(sac)_2(en)_2].2H_2O$ are systematically higher than those of [M(sac)₂(H₂O)₄].2H₂O indicates that ethylenediamine is a stronger ligand than water, which agrees well with the spectrochemical series.

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