SYNTHESIS AND CHARACTERIZATION OF SOME METAL COMPLEXES WITH NEW SCHIFF BASE LIGAND OF GLUTAMINE

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Abstract - In this paper, the new Schiff base ligand disalicyaldine succinoyl diglutamide (DSSG) was prepared from the reaction of the succinic anhydride with glutamine and then with salicyaldehyde. The prepared free Schiff base ligand was characterized by IR and electronic spectra, GC-mass spectrometer and elemental microanalysis (C.H.N.). The paper also included of prepared complexes through the reaction of the above ligand with metal ion salts (Cr^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2} and Cd^{+2}) under reflux using ethanol-water mixture as a solvent and potassium hydroxide as a base to prepare the complexes. These complexes were characterized by IR, electronic spectra, molar conductivity, magnetic susceptibility and flame atomic absorption (A.A) to determine the metal in complexes. The values of elemental microanalysis and metal contents were in a good agreement with the calculated values. The molar conductivity indicated that all these complexes were non-electrolyte nature, except chromium complex that had an electrolyte nature. The magnetic susceptibility indicated that all these complexes were paramagnetic except cadmium complex that was diamagnetic. According to the mentioned characterization methods, the following general geometrical structures were proposed to the complexes that that were tetrahedral around Co^{+2}, Ni^{+2}, Cu^{+2} and Cd^{+2} ions and octahedral around Cr^{+3} ion.

I. INTRODUCTION

The field of Bioinorganic Chemistry is very promising and versatile in the domain of Coordination Chemistry which is not only an important branch of chemistry but has become a separate branch of chemistry,this is because living systems depend for their existence on many coordination compounds in which metals ions are chelated by bioligand such as amino acids, the building blocks of proteins and their derivatives including several of their metabolic intermediates [1-3].

Coordination complexes, particularly chelates, play fundamental role in the biochemistry of both plants and animals, several of these complexes are based on proteins as the metal protein complexes play a vital part in metabolic path ways. Few products of natural origin are as versatile in their behavior and properties and few have such a variety of biological functions to perform as the amino acids and their derivatives [4-7]. In the metallo enzymes, the metal atom can be directly bounded to side chains of amino acids residues or to other ligands which are covalently linked to the protein [8-11].

Also elements form various complexes with amino acids, these complexes contributed in several metabolisims in human body,iron for example, plays an essential role in the biological molecules such as hemoglobin, myoglobin, ferrodoxin, and rubredoxin. Hemoglobin is found in red blood cells. It is the oxygen that transports protein of higher animals; myoglobin is the oxygen protein of skeletal muscle. The heme group is an essential component of these proteins. In the body the iron in the heme is coordinated to the four nitrogen atoms of a porphyrin and also coordinated to a nitrogen atom of ahistidine amino acid residue in the hemoglobin and myoglobin protein [12-15].

II. MATERIALS AND METHOD

The chemicals were of highest purity were purchased from Fluka, Sigma and Aldrich companies, distilled deionizer water were used for all research purposes, all the glassware were immersed in diluted 5% nitric acid for 24 hrs, then rinsed with four times with deionizer water.

The melting points were determined on Electro thermal, melting point 9300. IR spectra were recorded using KBr discs in the range (4000-400) cm^{-1} on FTIR (Shimadzu, IR-Prestige-21 FTIR 8400S). The electronic spectra of the free Schiff base ligand and its metal complexes were recorded in DMF solution, using Shimadzu model 160A UV-Vis. Spectrophotometer. Conductivity measurements of the metal complexes were recorded at 25^0C for 10^{-3}M solutions of the samples in DMF, using (Hand-Held Meter LF330). Flame atomic absorption Spectrophotometer was obtained by using Shimadzu 160AA. Elemental microanalysis for (C.H.N) were carried out on (Euro-vector EA3000A), University of Babylon. Magnetic susceptibility of the metal complexes were determined at 25^0C with magnetic susceptibility balance (Johson Matthey) in Al-Nahran University.

1. Preparation of SuccinoylDiglutamide:

Succinic anhydride (1gm , 10 mmole) was dissolved in absolut ethanol (10 cm^3). Glutamine (2.923 gm ,

20mmole) was dissolved in deionized water (20 cm^3) and then two drops of concentrated hydrochloric acid was added to the glutamine solution and this solution was added to the succinic anhydride solution. The mixture was heated under reflux at temperature (60ºC) for (15min) and immediately the precipitation of the white solid was complete .

Then, the solid collected by filtration , was washed with water (15 cm^3×2) and dried at temperature (50ºC) for three hours.

yield=85% , m.p = 168°C.

2. Preparation of DislicylaldeneSuccinoylDiglutamide:

Sodium hydroxide (0.4 gm , 10mmole) was dissolved in methanol (30 cm^3) and (2.076gm , 6mmole) of succinoyldiglutamide was added to the solution. The mixture was stirred at room temperature untile the mixture become homogenous. Salicylaldehyde (1.464 gm , 12 mmole) was dissolved in (5 cm^3) of absolute ethanol and then added to the mixture.

After two minutes the mixture was evaporated to 20% of its original volume and (1cm^3) of acetic acid was added immediately . After two hours, light yellow crystal was appeared. Then the solid collected by filtration , was washed with ethanol (15 cm^3×2) , and then recrystallized from (ethanol - water) (1 :1) mixture. The yellow powder was collected by filtration and then dried at temperature (50ºC) for three hours.

3. Preparation of DisalicylaldeneSuccinoylDiglutamide Complexes:

DisalicylaldieneSuccinoylDiglutamide (0.526 gm ,1 mmole) was dissolved in deionized water (10 cm^3) . The metal salt copper acetate (0.399 gm ,2 mmole) , Cobalt nitrate (0.582gm , 2 mmole) , chromium nitrate (0.800gm , 2 mmole) , Nickel chloride (0475gm , 2 mmole) , Cadmium nitrate (0.616gm , 2 mmole) respectively ; each of them was dissolved in absolute ethanol (10 cm^3).

Each of the metal solution was added to the organic solution (ligand solution) with stirring and (2cm^3) of (0.2 M) potassium hydroxide was added to the mixture of each complex except in the case of copper complex. The mixture was heated under refluxe at temperature (70 -80ºC) for four hours.

During this period, the solid changed to violet , deep pink , dark gray , bluish green and off white respectively . The colour solid for each complex was then collected by filtration , washed with ethanol (10 cm^3×2) , and then recrystallized from ethanol - deionized water (1 : 1) mixture . The colour crystals were collected by filtration and then dried at temperature 50ºC for three hours.

III. RESULTS AND DISCUSSION

1. Physical properties of the free Schiff base ligand and their complexes

The new is good coordination ligands due to the fact that it is consist of hard nitrogen atom as well as hard oxygen atom in the same structure.

The important of preparing a new (DSSG) ligand from its Virility as starting material for the synthesis many complexes especially with some light transition metal ions. Table (1) shows the physical data for the new ligand and its complexes they showed different melting points and colors. The molar conductance measurements suggested the absence of anion (chloride or nitrate) outside the coordination sphere for nickel (II) complex, cobalt (II) complex, copper (II) complex and cadmium (II) complex which indicated that metal complexes are non-electrolytic nature. The molar conductance of the chromium (III) complex reveals the presence of nitrate ion outside the coordination sphere which indicated that the chromium (III) complex has an electrolytic nature.

The metal forms ratio 2:1 complexes with Schiff base ligand. Measuring magnetic susceptibility contributes in the determination of structure of the complexes. These measurements provide information about the type of bonding and strength of the ligand field of complexes and also give information about the number of unpaired electrons. The magnetic momentums of chromium (III) d^3, and cobalt (II) d^3 complexes were found to be (3.96, 3.97) B.M., respectively within the expected spin only values.

Moreover, the higher value of the magnetic momentum for nickel (II) d^8 complexes was found to be (3.87) B.M. which is due to the orbital contribution [16]. The magnetic momentum for copper (II) d^9 complex was found to be (1.95) B.M. within expected value for one electron. Finally, the magnetic momentum for cadmium (II) d^{10} complex is diamagnetic as expected from its electron configuration. From the above values, it is indicated that all the metal complexes are paramagnetic (high spin) except the cadmium complex that is diamagnetic [17].

The microanalysis (C.H.N) and metal contents of the free Schiff base ligand and its metal complexes were obtained using (Euro vector EA3000 single V.3.0 single) and flame atomic absorption Spectrophotometer (Shimadzu 680 A). The data of the free Schiff base ligand and its metal complexes were in good agreements with the calculated values, which indicated the identities and purities of the ligand and its metal complexes. All these data are summarized in Table(1).

Compound	Yield%	Color	m.p.(^{0}C)	Molar rati M:L	M% (calc.) found	M.Wt g.mole^{-1}	Microanalysis (Cal.) Found C	H	N	Molar conductance μ_s.Cm^{-1}	μ_{eff}(B.M)
DSSG	84	Yellow	165	--		526	(57.73) 58.31	(5.15) 5.34	(9.62) 10.30	-----	-----
$[Cr_2(DSSG)(H_2O)_4](NO_3)_2$	76	Dark gray	200	2:1	(13.686) 14.614	760	(41.1) 40.01	(4.47) 40.4	(7.4) 8.33	199.00	3.96
$[Co_2(DSSG)]$	70	Deep pink	180	2:1	(18.422) 17.360	640	(48.28) 47.52	(40.05) 4.34	(8.08) 8.31	153.5	3.97
$[Ni_2(DSSG)]$	72	Bluish-green	182	2:1	(18.35) 18.894	640	(48.32) 49.03	(3.74) 3.88	(8.8) 9.01	92.4	3.87
$Cu_2[DSSG)]$	78	Violet	170	2:1	(19.64) 18.211	647	(48.4) 48	(4.02) 4.01	(8.65) 8.41	24.00	1.95
$[Cd_2(DSSG)]$	64	Off white	220	2:1	(28.005) 27.368	746.8	(41.85) 41.37	(1.99) 2.04	(7) 7.27	35.6	0.0

Table-1-Pysical properties, analytical data, molar conductance and magnetic moments of the ligands and its complexes:

2. Infrared Spectra of DisalicyladineSuccinoylDiglutamide(DSSG) and its metal complexes

The infrared frequencies of the free Schiff base ligand and its metal complexes are compiled in Table (2).

The infrared spectrum of the free Schiff base ligand is compared with that of the complexes to determine the coordination sites that may have involved in the complexation. The spectrum of the free Schiff base ligand which is illustrated in figure (1) shows the medium bands at 3408, 3321 , 3271 and 3174cm^{-1} [18,19] which are assigned to the stretching vibration of (N-H) due to intramolecular hydrogen bonding. The absorption band about 3000 cm^{-1} is assigned to the stretching vibration of (C-H) aromatic, while the absorption bands at 2933 and 2879 cm^{-1} are assigned to the stretching vibration of (C-H) aliphatic a symmetrical and symmetrical respectively. The strong absorption bands at 1687 and 1635cm^{-1} due to the stretching vibration of (C=O) [19].

The absorption band at 1585cm^{-1} which is assigned to the azomethine group (C=N). The stretching vibration band for (C-O) and (C-N) observed at 1203 and 1130 cm^{-1}, respectively. The spectra of the metal complexes showed bands at range (3342-3115) cm^{-1} assigned to the stretching vibration of (N-H) due to the intramolecular hydrogen bonding [18] which indicated the non involvement of the (N-H) for coordination. The (C = N) band at (1585) cm^{-1} in the spectrum of the free Schiff base ligand, shifted to lower frequencies in the spectra of all metal complexes in the range between (1508-1573) cm^{-1} which indicated the coordination of the ligand through nitrogen atom of the azomethine group.

The band (C -O) at (1687) cm^{-1} in the spectrum of the free schiff base ligand , shifted to lower frequencies in the spectrum of chromium , cobalt , nickel , copper complexes in the range (1687- 1662) cm^{-1} and shifted to higher frequency in the spectrum of cadmium complex as shown in figure (2) which indicated the coordination of the ligand through oxygen atoms of the carboxylic group [19].

The IR specturm of chromium Complex has a broad band at region (3406)cm^{-1} and (825)cm^{-1} assigned to the stretching Vibration of (OH) of water indicated the presence of two water molecules in the Crystal lattice of the chromium complexes [20].

Also the IR spectrum of chromium complex has weak band at (859) cm^{-1}which was assigned to the presence of nitrate ion outside the coordination sphere. This is illustrated in figure (3) [19].

New bands appeared in the spectra of metal complexes at (457-486) cm^{-1}and (497-549) cm^{-1} which are assigned to the stretching vibration of (M-O) and (M-N), respectively.

Compound		υ(C-H)ar.	υ(C-H)al.	O // υ (C-O)	υ (C=O)	υ(C=N)	υ(C-O)	υ(C-N)	υ(M-O)	υ(M-N)
(DSSG)	(3408-3174)	3000	2933	1687	1635	1585	1203	1130	-	-
$[Cr_2(DSSG)(H_2O)_4](No_3)_2$	(3406-3221)	3000	2972	1674	1635	1537	1201	1161	457	516
$[C_{O2}(DSSG)]$	(3442-3115)	3000	2927	1660	1625	1508	1211	1161	480	528
$[Ni_2(DSSG)]$	(3394-3250)	3000	2950	1660	1620	1550	1219	1166	464	505
$[Cu_2(DSSG)]$	(3398-3140)	3000	2966	1662	1618	1573	1232	1159	486	549
$[Cd_2(DSSG)]$	(3441-3278)	2966	2943	1762	1624	1558	1230	1153	462	497

Table -2- Infrared spectra data of the free ligand (DSSG) and its metal complexes

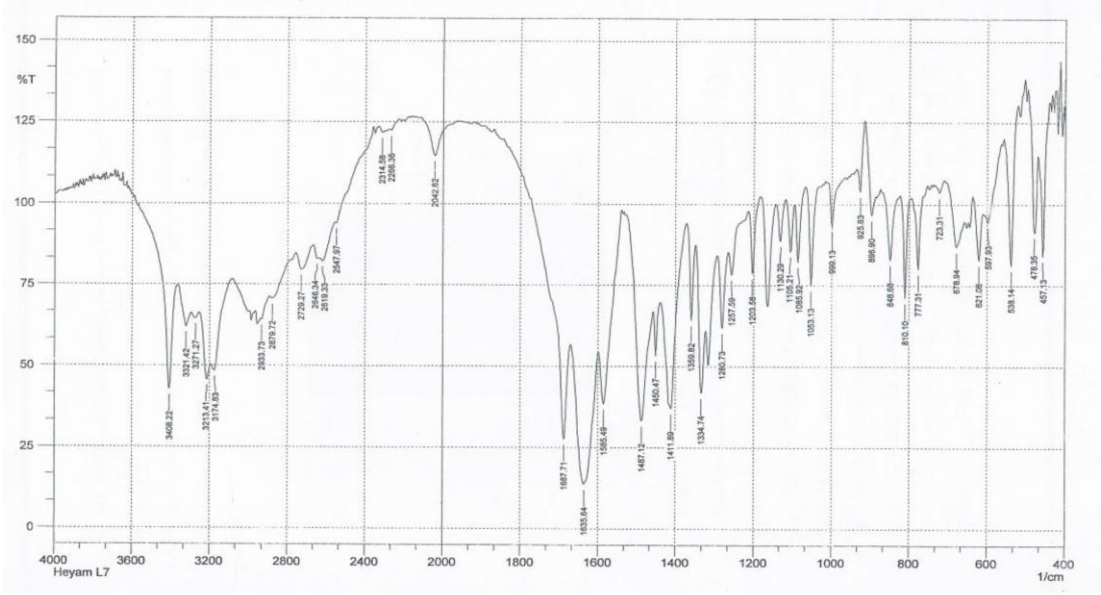


Figure (1) Infrared spectrum of disalicylaldineSuccinoylDiglutaminide(DSSG)

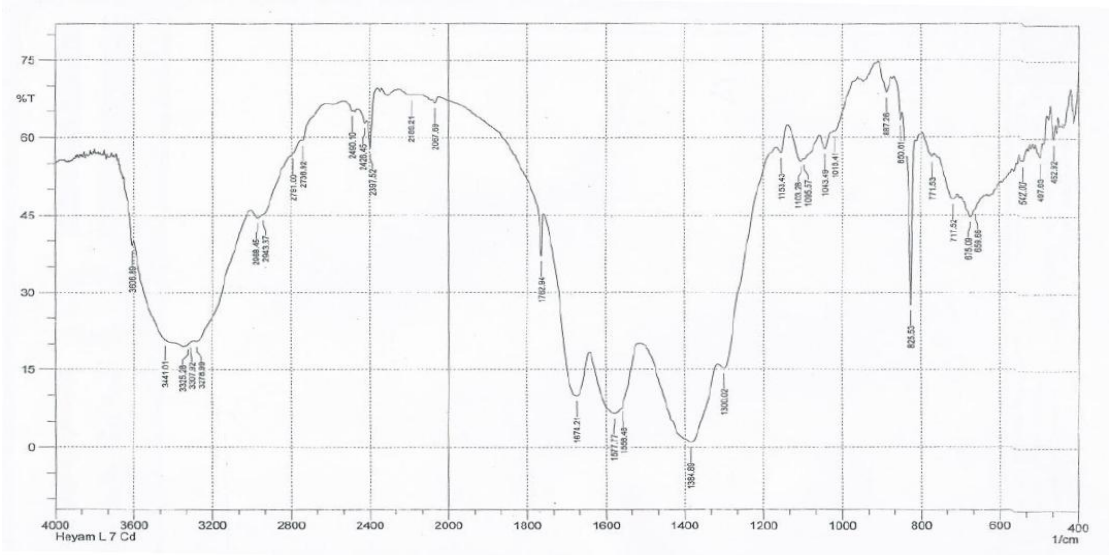


Figure (2) Infrared spectrum of [Cd2(DSSG)] complex.

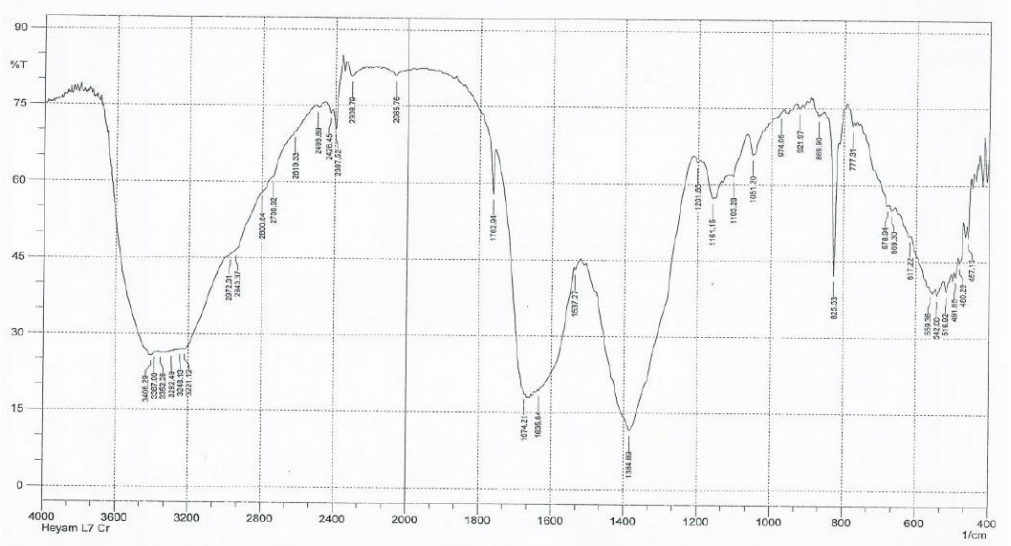


Figure (3) Infrared spectrum of $[Cr_2 (DSSG)(H_2O)_4](NO_3)_2$complex.

3. Electronic Spectra of DisalicyaldineSuccinoylDiglutmide (DSSG) and its Metal Complexes

Most of transition metal complexes are colored and their colors are different from the trasition metal salts and the ligands. This is an important indication of coordination; therefore, the colored complexes showed different characteristic absorption bands in their position and intensity [21,22]. All the spectra of the free Schiff base ligand (disalicyaldinesuccinoylglutmide) and its metal complexes were summarized in Table (3) and Figures (4), (5), (6), (7), (8) and (9). The spectrum of the free Schiff base ligand shows one high intensity absorption band at 325 nm (30769 cm^{-1}) which was assigned to (π-π^*) transition. The spectrum of chromium (III) complex shows four bands, the first one appears at 304 nm (32895 cm^{-1}) due to (π-π^*) transition, the other three bands appeared at 386 nm (25907 cm^{-1}), 558 (17921 cm^{-1}) and 670 nm (14925 cm^{-1}) due to charge transfer, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{2g}$, respectively. These transitions were characterized to octahedral geometry around the chromium ion [23, 24]. The spectrum of cobalt (II) complex, showed three bands, the first one strong band showed at 304 nm (32895 cm^{-1}) assigned to (π-π^*) transition, the other bands showed at 370 nm (27027 cm^{-1}) and 533 nm (18762 cm^{-1}) respectively can be assigned to charge transfer transition for the cobalt complex [25] and $^4A_2 \rightarrow {}^4T_1(P)$, suggesting the tetrahedral geometry around the cobalt ion. The spectrum of nickel (II) complex showed four bands one of them appeared at 306 nm (32680 cm^{-1}) assigned to (π-π^*) transition, the other showed at 362 nm (27624 cm^{-1}), 435 nm (22989 cm^{-1}) and 620 nm (16129 cm^{-1}) assigned to charge transfer, $^3T_1 \rightarrow {}^1T_2$ and $^3T_1 \rightarrow {}^3T_1(P)$ suggesting tetrahedral structure about nickel ion. In the copper (II) complex the mainly sing broad band is shown at 606 nm (16502 cm^{-1}) which is a characteristic of tetrahedral of copper (II) complex. Because the d^9 configuration can be thought of as an inversion of d^1 relatively simple spectrum consisting of a single broad band is expected for d^9 complex [26]. This band is due to $^2T_2 \rightarrow {}^2E_1$.

The bands are at 304 nm (32895 cm^{-1}) and 410 nm (24390 cm^{-1}) to (π-π^*) and charge transfer respectively. The spectrum of cadmium (II) complex shows two bands at 304 nm (32895 cm^{-1}) and 349 nm (28653 cm^{-1}) due to (π-π^*) and charge transfer (C.T.), respectively. The absence of (d-d) electronic transition in the cadmium complex is due to the configuration (d^{10}) structure for the metal ion, suggesting tetrahedral for the SP^3 hybridization of cadmium [27].

Compound	λmax(nm)	Wave number (cm^{-1})	Absorbance	Emax $L.mol^{-1}.cm^{-1}$	Assignments	Suggested structure
(DSSG)	325	30769	0.891	891	π-π^*	-
$[Cr_2(DSSG)(H_2O)_4](NO_3)_2$	304 386 558 670	32895 25907 17921 14925	1.519 1.122 0.560 0.264	1519 112 560 264	π-π^* C.T. $^4A_2g \rightarrow {}^4T_1g(F)$ $^4A_2g \rightarrow {}^4T_2g$	Octahedral
$[Co_2(DSSG)]$	304 370 533	32895 27027 18762	1.8 0.932 0.396	1800 932 396	π-π^* C.T. $^4A_2 \rightarrow {}^4T_1(P)$	Tetrahedral
$[Ni_2(DSSG)]$	306 362 435 620	32680 27624 22989 16129	0.248 0.345 0.119 0.11	248 345 119 110	π-π^* C.T. $^3T_1 \rightarrow {}^1T$ $^3T_1 \rightarrow {}^3T_1(P)$	Tetrahedral
$[Cu_2(DSSG)]$	304 410 606	32895 24390 16502	0.726 0.521 0.522	726 521 522	π-π^* C.T. $^2T_2 \rightarrow {}^2E$	Tetrahedral
$[Cd_2(DSSG)]$	304 349	32895 28653	0.100 0.252	100 252	π-π^* C.T.	Tetrahedral

Table -3- Electronic spectra data of free ligand (DSSG) and its metal complexes

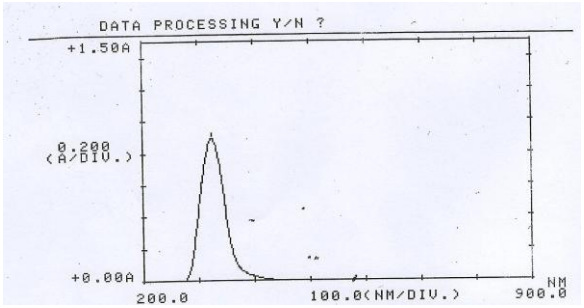


Figure (4) Electronic Spectrum of DisalicyaldineSuccinoylDiglutmide(DSSG)

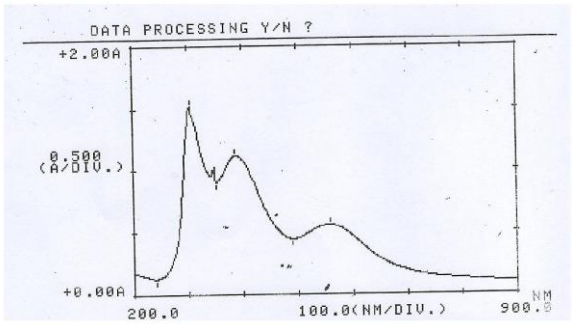


Figure (5) Electronic Spectrum of $[Cr_2(DSSG)(H_2O)_4](NO_3)_2$ complex.

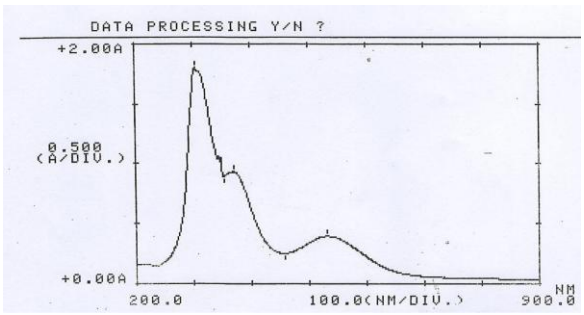


Figure (6) Electronic Spectrum of $[Co_2(DSSG)]$ complex.

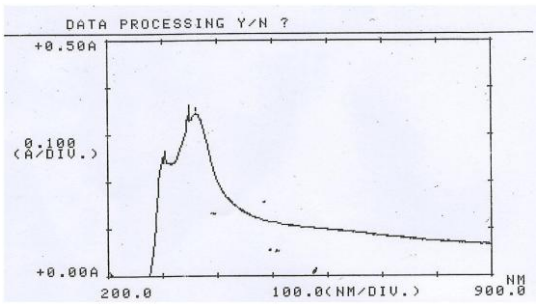


Figure (7) Electronic Spectrum of $[Ni_2(DSSG)]$ complex.

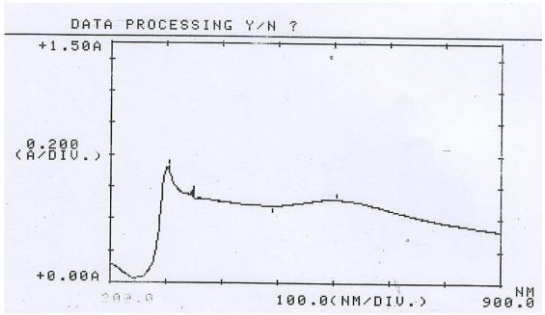


Figure (8) Electronic Spectrum of $[Cu_2(DSSG)]$ complex.

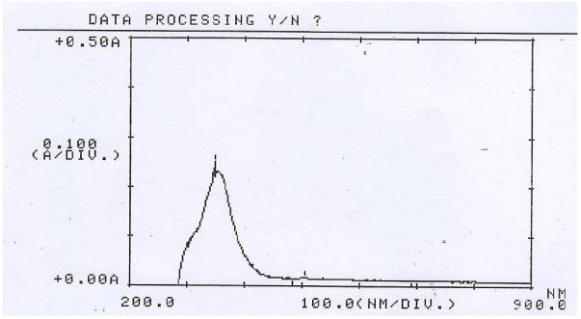
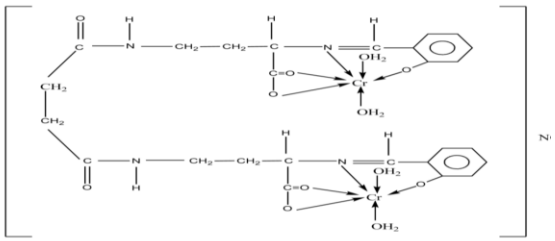
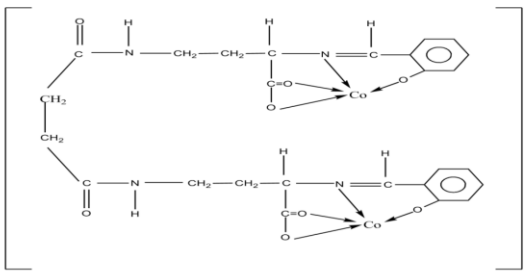


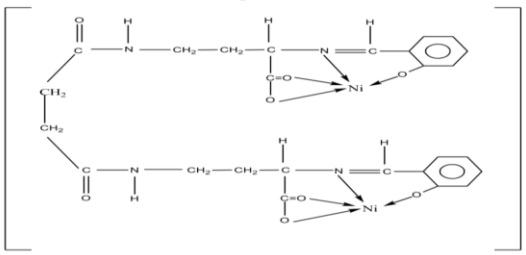
Figure (9) Electronic Spectrum of $[Cd_2(DSSG)]$ complex.



$[Cr_2(DSSG)(H_2O)_4]NO_3$



$[Co_2(DSSG)]$



$[Ni_2(DSSG)]$

REFERENCES

[1] S. ajith Sinthuja, "Synthesis and spectroscopic characterization of amino acid based schiff base ligands and its complexes as microbial growth inhibitors." ijrpc 8(1), pp.52-60 , 2018.

[2] Siham Slassi, Adeline Fix-Tailler, Gérald Larcher, Amina Amine, and Abdelkrim El-Ghayoury, "Imidazole and Azo-Based Schiff Bases Ligands as Highly Active Antifungal and Antioxidant Components," Heteroatom Chemistry, vol. 8 pages?, 2019.

[3] lucia lintnerová , jindra valentová , ferdinand devínsky ," antiradical activity of glutamine, l-asparagine and l-aspartic acid derived reduced schiff base copper(ii) complexes" studia ubb chemia, lxi, 4, pp. 85 - 98. 2016.

[4] Muthusamy Selvaganapathy1 and Natarajan Raman2 '' Pharmacological Activity of a FewTransition Metal

Complexes: A Short Review'' J Chem Biol Ther, Vol 1(2): 108, 2016.

[5] Disha Sharma , Hosakere Doddarevanna Revanasiddappa , Basappa Chidanda Vasantha Kumar , Basavegowda Jayalakshmi , Nangappagowda Dharmappa Rekha .'' Co(III) and VO(IV) complexes with a new bidentate Schiff base: Interaction with BSA and antimicrobial studies'' Biointerface Research in Applied Chemistry. Volume 9, Issue 1, 3776 - 3782, 2019.

[6] Md. Saddam Hossain, Pijush Kanti Roy, CM Zakaria and Md. Kudrat-EZahan.'' Selected Schiff base coordination complexes and their microbial application: A eview International Journal of Chemical Studies; 6(1): pp.19-31.2018

[7] Georgiy B. Shul'pin , Debbie C. Crans , Luísa M. Martins , Kamran T. Mahmudov . ''Preface Coordination compounds and catalysis'' Coordination Chemistry Reviews . vol. 380,p. 600, Feb. 2019.

[8] LeuchtenB. W.; Huth,M. K.; Drauz, K. . Current status and prospects. Applied Microbiology and Biotechnology 69(1): 1-8.2005.

[9] M.Fazal-ur-Rehman , Nagina Naveed Riaz.'' Biological Applications of β-amino acids and its derivatives'' International Academy of Engineering and Medical Research, Vol-2, Issue-7.2017.

[10] M.Fazal-ur-Rehman.'' Biological Scope of β-amino Acids and its Derivatives in Medical Fields and Biochemistry: A Review. '' Med Chem 8: 95-98.2018.

[11] Mehdi Mirzaie.'' Discrimination power of knowledge-based potential dictated by the dominant energies in native protein structures''Amino acids . pp.1-10. May 2019.

[12] Lin , Z.; Robledo , J.A. ''metals and membrane metal transporters in biological systems: the role(s) of nramp in host-parasite interactions'' .. J. Argent . Chem. Soc., 97(1) : 210 -225.2009 .

[13] Kocabas E, Hernick M (2013) Metalloenzymes: Use of Recombinant Protein Expression and Affinity Tags to Aid Identification of Native Metal Ion Cofactors. Biochem Anal Biochem 2:132.2013 .

[14] Thiago M. A. Santos , Matthew G. Lammers , Maoquan Zhou†, Ian L. Sparks Madhusudan Rajendran , Dong Fang , Crystal L. Y. De Jesus , Gabriel F. R. Carneiro , Qiang Cui , and Douglas B. Weibe.'' Small Molecule Chelators Reveal That Iron Starvation Inhibits Late Stages of Bacterial Cytokinesis''. ACS Chem Biol. 19; 13(1): 235–246. January2018.

[15] Wilfred R. Hagen, Peter-Leon Hagedoorn and Kourosh Honarmand Ebrahimi .'' The workings of ferritin: a crossroad of opinions'': Metallomics, 9, 5, pp. 595--605, 2017.

[16] Shayma, A.S.; Mohammed, H.A.; Al – Hamadani A. A.S. (2010). J. basic. App. Sci. 4: 5178-5183.

[17] Gary, L.; Donald , A. (2010). 4th Ed- Inorganic Chemistry. Prentic – Hall. Inc.

[18] Souza, P.; Jose, A.; Vazguez, G.; and Masaguer, J.R. (1985). Trans. Met. Chem. 10.410.

[19] Kellner, R.; Otto, M.; Widmer, H.W. (1998). Analytical chemistry. Wiley-VCH. USA

[20] Suresh, M.S.; Prakash, V. (2011). Int. J. current. 3.268-275.

[21] Gebbink, R.J.; Jones, R.J.; and Goldsmith, T.D. (2002). Inorg. Chem. 41:4633.

[22] Lever, A.B. (1984). 2nd Ed. Inorganic Electronic Spectroscopy. Elsvier publishing. New York.

[23] 23- Sutton, D. (1969). 1st ed. Electronic spectra of trans. Met. Complex. McGraw-Hill Publi Co. Ltd. New York.

[24] 24- Waheed, E.J. (2008). M.SC. Thesis, University of Baghdad, College of Education (Ibn-Al-Haitham).

[25] 25- Erdem, E.Y.; Sari, R.; Kilin, C. (2009). Trans. Met. Chem. 34:167-174.

[26] 26- Thahira, B.S.; Crouse, A.; Ibrahim, M. (2007). Polyhedron. 26(6): 1159-1165.

[27] 27- Numan, A.T.; Sultan, K.M.; and Abdullah, S.A. (2009). Polyhedron. Vol 22(3).

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