



Synthesis and Characterization of Complexes of New Derivative of Cyclopentaphenanthren-3-one with Manganese (II), Iron (II), Cobalt (II), Nickel (II), and Copper (II) Ions

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KEY WORDS

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ABSTRACT

This work involves the chemical preparation from a series of metal Complexes having the general composition $M(L)_2(H_2O)_2$, where $M = [Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}$ and $Cu^{+2}]$.

The ligand used was 9-fluoro-17-(1-hydrazono-2-hydroxyethyl)-11,17-dihydroxy-10,13,16-trimethyl-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3H-cyclopenta[a]phenanthren-3-one (FHDTCP), who was diagnosed by H-NMR spectra.

These complexes have been prepared and characterized by the ligand to metal by molar conductance, spectral (UV-Visible and FT-IR), and atomic absorption studies. The IR spectral measurements forecast interference to oxygen, nitrogen in coordination from the electron pairs to the metal ion in the center. And suggested the complexes geometry be octahedral for all.

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1. INTRODUCTION

Dexamethasone is a type of corticosteroid medication [1]. It is used in the treatment of many conditions, including rheumatic problems, a number of skin diseases, severe allergies, asthma, chronic obstructive lung disease, croup, brain swelling, and antibiotics in tuberculosis [2].

It is against deflation but the mechanism in which it works is unknown. Dexamethasone used in the treating of many conditions, such as severe allergies and many skin diseases, hematological conditions, asthma and chronic obstructive lung disease, brain edema, swelling, and anti TB drug [1,2]. In adrenocortical deficiency, it should be used collected with a medication that has grander Infectious crustaceans' powers like fludrocortisone [3]. In preterm labor, it perhaps used to increase child health. It may be taken by mouth, as an injection into ain concert, or to direct blood intravenously. The results of dexamethasone are mostly seen within a day to 3 days [1].

The long-standing use of dexamethasone perhaps affects bone loss, Damage to the lens of the eye, muscle weakness and the sensation of light bruises. It has been tested on pregnant women in the United States and has not been harmful [2]. In Australia, it has been used frequently in pregnant women and has not caused problems for babies [3]. There is a fear of using it during breastfeeding because it is anti-inflammatory and works to inhibit immunity [1].

Dexamethasone was included in the World Health Organization's List of Essential drugs after it is first manufactured in the year 1957 [4,5]. Dexamethasone is not expensive. It is used safely in most countries of the world and is inexpensive to the individual around the world [6].

In this work, I tried to find out the appropriate conditions for obtaining complications from this compound with different elements and this opens the way for studying how effective it is within the human body [3,4].

2. EXPERIMENTAL

I. Physical measurements

UV-visible spectra were recorded with a 160A Shimadzu spectrophotometer in the range of 200-1000 nm, and ethanol was used as a solvent. Metal contents of the complex were determined using a method suggested by [7,8].

The FTIR spectra were measured using FTIR 8300 Shimadzu Spectrophotometer in the range; 200-400 cm^{-1} as cesium iodide disc.

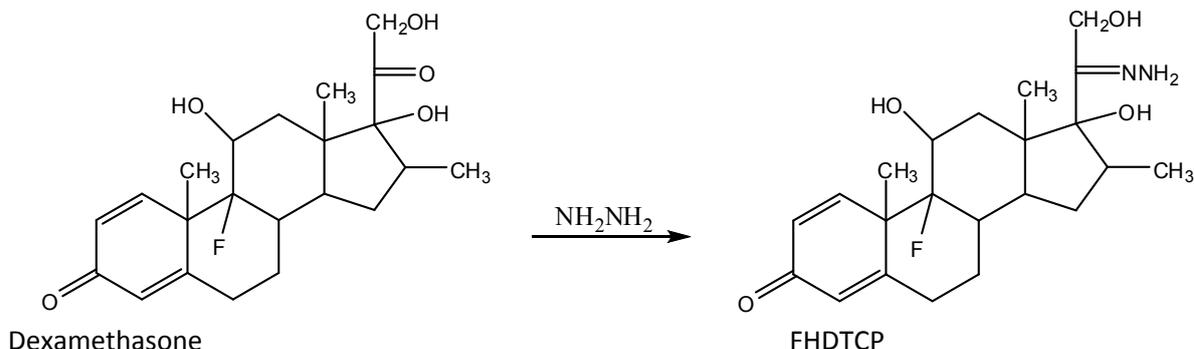
Metals were analyzed by using A680G atomic absorption Spectrophotometer. Melting points were determined by Gallencamp (M.F.B.600.010 F) melting point apparatus.

II. Materials

All reagents included in this work were of general-purpose grade and used without further purification.

III. Synthetic of Ligands

Dexamethasone (5 g, 13 mmol) is dissolved in ethanol 10 ml and treated with hydrazine hydrate (5ml, 8 mmol), and then the mixture was refluxed for 3 hours. The resulting solid was filtered off, dried and recrystallized from ethanol, as shown in Scheme (1):



Scheme 1: Preparation of the ligand (FHDTCP)

IV. Synthesis of Metal Complexes (General Procedure)

A mixture of metal [Mg^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} and Cu^{+2}] solution (1mmol) and the ligand FHDTCP (2 mmol) in ethanol at pH 8-9 was refluxed for 6 hours. The closed complexes were clarified with water, ethanol and under vacuum was dried [9].

3. PHYSICAL PROPERTIES OF THE COMPLEXES

The ligand is bonding with the metal ions to form the complexes were studied in ethanol (or DMF), the molar ratio method is pursuing in to decide the order (M: L) ratio in the complex and [10]. Mixture set of varying concentration of the ligand FHDTCP and constant concentration of the metals (1 mmol) [Mg^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} and Cu^{+2}]. The mole ratio [M/L] can be determined from plotting the absorption at a λ_{max} wavelength and molar ratio of [M/L]. The determined values of [M/L] were presented at Table 1.

TABLE I: The measured physical properties of the ligand and its complexes.

No.	Structure	Mole Ratio	Color	M. p (°C)	Conductivity ($\mu s.cm^{-1}$)*	Yield	Elemental analysis M%	
							Calc.	Found
L	FHDTCP	-	Orange	260-262	-	80	-	-
[Mn(L) ₂ (H ₂ O) ₂]	FHDTCP-Manganese(II) di aqua	1:2	Brown	> 300	5	85	6.4	7.1
[Fe(L) ₂ (H ₂ O) ₂]	FHDTCP-Iron(II) di aqua	1:2	Green	> 300	12	89	6.5	6.8
[Co(L) ₂ (H ₂ O) ₂]	FHDTCP-Cobalt(II) di aqua	1:2	Yellow	>300	7	78	6,8	7.3
[Ni(L) ₂ (H ₂ O) ₂]	HDTCP-Nickel(II) di aqua	1:2	Yellow	98-100	3	80	6.8	7.0
[Cu(L) ₂ (H ₂ O) ₂]	FHDTCP-copper(II) di aqua	1:2	Dark Brown	150-155	6	81	7.3	7.6

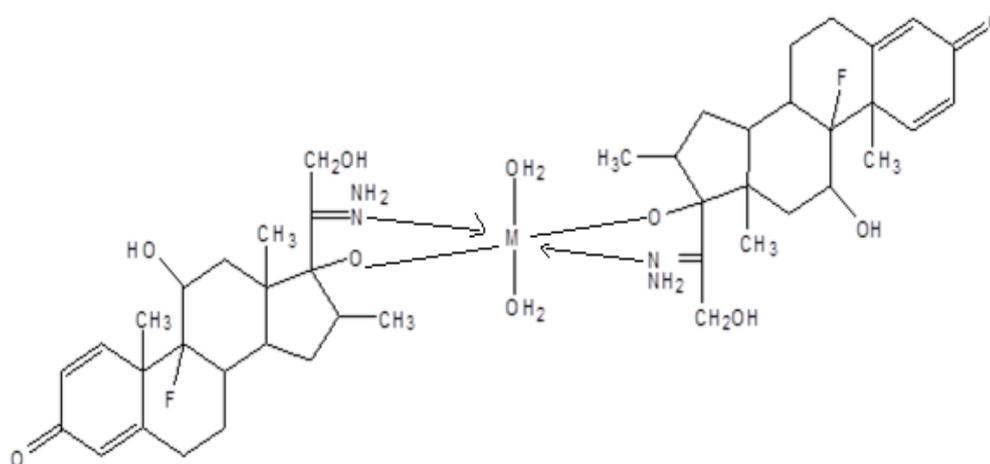
*DMSO solvent used to measured conductivity at room temperature (25 ° C). Where (0-20) are non-conductive; (20-40) are unknown; (40-60) are conductive ⁽¹¹⁾.

4. RESULTS AND DISCUSSION

The ligand has been obtained by the reaction of dexamethasone with appropriate hydrazine hydrate in ethanol, as in Scheme 2. It was found that all the prepared complexes the ligand FHDTCP behave as a bidentate ligand, and coordinate through oxygen and nitrogen donor atoms. All complexes were found to be paramagnetic in nature. The other analytical data and spectral results were found to support the octahedral structure around the central metal atom. All the complexes were found soluble in common organic solvents like ethanol, methanol, CCl₄, DMSO, and DMF, but they were found insoluble in ether, water, acetone, and benzene.

The molar ratio method was followed to identify the equivalency of metal ion coordination to ligands for the prepared complexes in ethanol.

The [M/L] ratio was found to be 1:2 for all the complexes. The molar conductance values of ($1*10^{-3}$ M) solutions of [M(L)₂(H₂O)₂] type of complexes in the range $5-15 \Omega^{-1} cm^2 mol^{-1}$ in DMF indicating their non-polar properties (where [M = Mn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2}]; L = FHDTCP



M = (Mn⁺², Fe⁺², Co⁺², Ni⁺², Cu⁺²)

Scheme 2: The suggested structure of the complexes [M(FHDTCP)₂(H₂O)₂]

I. FT-IR spectra

In mandate to get information about the coordination behavior of the ligands with the transition metal complexes, a comparison of the FT-IR spectra of the ligands and their metal complexes has been made (table 1). The stretching vibration pack of $\nu(\text{C}=\text{O})$ denoted at 1720 cm^{-1} in the free ligands (L) were shifted to lower frequencies 1649 cm^{-1} , 1653 cm^{-1} , 1645 cm^{-1} , 1647 cm^{-1} and 1700 cm^{-1} for L complexes where [M = Mn⁺², Fe⁺², Co⁺², Ni⁺² and Cu⁺²] respectively which indicate the linkage of the ligands to the metal ions [13].

The weak absorption bands attributed to the $\nu(\text{-CN})$ of the imine group were observed at 2264 cm^{-1} for the ligand. These bands were moved to lower frequencies by 2220 cm^{-1} , 2240 cm^{-1} , 2220 cm^{-1} , 2215 cm^{-1} and 2210 cm^{-1} in the spectra of complexes where [M = Mn⁺², Fe⁺², Co⁺², Ni⁺² and Cu⁺²] which indicates the coordination of the ligand to the metal ion from which one of the nitrogen atoms at the imine collection which enters into coordination when unshared electron pair of one nitrogen atom of an imine group has been utilized in covalent linkage to a metal atom. The electrometric effect will render the unshared electron pair of the second nitrogen atom less available for attachment to a metal atom [14]. The position of the rest of the IR bands is cited in the table (2).

TABLE II: Particular FT-IR bands in cm^{-1} for the ligand and their complexes

Compound	$\nu\text{C-H Ar.}$	$\nu\text{C-H Aliph.}$	$\nu\text{C}=\text{C Ar.}$	$\nu\text{N}=\text{N}$	νCN	$\nu\text{C}=\text{O}$	$\nu\text{M-O}$	$\nu\text{M-N}$
L	3115	2937	1564	1461	2264	1720	-	-
[Mn(L) ₂ (H ₂ O) ₂]	3028	2888	1572	1445	2220	1649	613	511
[Fe(L) ₂ (H ₂ O) ₂]	3008	2915	1570	1480	2240	1653	513	434
[Co(L) ₂ (H ₂ O) ₂]	3020	2906	1568	1481	2220	1645	515	451
[Ni(L) ₂ (H ₂ O) ₂]	2987	2912	1570	1442	2215	1647	540	424
[Cu(L) ₂ (H ₂ O) ₂]	3013	2905	1574	1464	2210	1700	530	425

II. UV/visible spectra

The UV-vis. spectral facts for the ligands and their metal complexes in the solid-state in nujol are given in tables (3). The absorption bands that appeared in the UV region are attributed to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) electronic transitions in the aromatic ring of the ligands and their metal complexes. Additional bands that appeared at higher wavelengths may be attributed almost to transitions in the d-orbitals of the metal [15].

- 1) **The UV spectra of Ligand only (L);** The continuum of at liberty ligand L viewings a strong band at (258) nm which may perhaps be recognized to ($\pi \rightarrow \pi^*$) and another at (370) nm suitable to ($n \rightarrow \pi^*$) [15].
- 2) **The UV spectra of brown Manganese (II) complex (L);** showed two spins allowed transitions at (340 and 342) nm assignable to (${}^6A_{1g} \rightarrow {}^4T_{1(p)}$) (p) and (${}^6A_{1g} \rightarrow {}^4E_g$) (D) transitions sequentially, agree with octahedral arrangements for (Mn^{+2}) [15].
- 3) **The UV spectra of green Fe (II) complex (L);** showed the spectral band at (202) nm suitable to ($\pi \rightarrow \pi^*$) transition and any more band at (341) nm which caused by the (d-d) transitions were obscured by intense charge transfer bands, assignable to (${}^5T_{2g} \rightarrow {}^5E_g$) transition agrees with octahedral arrangements for (Fe^{+2}) [16].
- 4) **The UV spectra of dark yellow Cobalt (II) complex (L);** The electronic spectrum of dark yellow complex confirmations a band at (240) nm may be suitable to charge transfer. The other band at (305) nm may be ascribed to (${}^4A_{2(F)} \rightarrow {}^4T_{1(p)}$) (v3), and the electronic transition of (${}^4A_{2(F)} \rightarrow {}^4T_{1(F)}$) (v2), is an institute at (306) nm. At last, the absorption band at (680) nm is suitable to (${}^4A_{2(F)} \rightarrow {}^4T_{2(F)}$) (v1), sequentially agree with octahedral arrangements for (Co^{+2}) [17].
- 5) **The UV spectra of yellow Ni (II) complex (L);** The electronic spectrum of a yellow complex of Ni (II) viewings band at 241 nm suitable to charge relocation. The other mobs at (343, 561) nm may be attached to (${}^3A_{2(F)} \rightarrow {}^3T_{1(F)}$) and (${}^3A_{2(F)} \rightarrow {}^3T_{1(p)}$) sequentially agree with octahedral arrangements for (Ni^{+2}) [18].
- 6) **The UV spectra of yellow Cu (II) complex (L)** The electronic spectrum of dark brown of (Cu^{+2}) shows a band at 322 nm suitable to duty transfer. The other crowds at (304) nm may be attributed to (${}^2B_{1g} \rightarrow {}^2A_{2g}$), (${}^2B_{1g} \rightarrow {}^2B_{2g}$), and (${}^2B_{1g} \rightarrow {}^2E_g$) sequentially agree with octahedral arrangements for (Cu^{+2}) [17].

TABLE III: Electronic spectra for the ligand and its complexes.

Compounds	λ nm	ABS	Transitions
L	258	-0.023	$\pi \rightarrow \pi^*$
	289	-0.038	$\pi \rightarrow \pi^*$
	370	-0.016	$n \rightarrow \pi^*$
[Mn(L) ₂ (H ₂ O) ₂]	211	-0.057	C.T
	253	-0.012	
	340	-0.006	${}^6A_{1g} \rightarrow {}^4T_{1(p)}$
[Fe(L) ₂ (H ₂ O) ₂]	342	-0.002	${}^6A_{1g} \rightarrow {}^4E_{g(D)}$
	202	-0.0202	C.T
	341	-0.341	${}^5T_{2g} \rightarrow {}^5E_g$
[Co(L) ₂ (H ₂ O) ₂]	240	-0.076	C.T
	305	-0.096	${}^4A_{2(F)} \rightarrow {}^4T_{1(p)}$ (v3)
	306	-0.098	${}^4A_{2(F)} \rightarrow {}^4T_{1(F)}$ (v2)
[Ni(L) ₂ (H ₂ O) ₂]	680	-0.008	${}^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ (v1)
	241	-0.064	C.T
	343	-0.075	${}^3A_{2(F)} \rightarrow {}^3T_{1(F)}$
[Cu(L) ₂ (H ₂ O) ₂]	561	-0.064	${}^3A_{2(F)} \rightarrow {}^3T_{1(p)}$
	322	-0.385	${}^2B_{1g} \rightarrow {}^2A_{2g}$
	304	-0.367	${}^2B_{1g} \rightarrow {}^2B_{2g}$
	306	-0.153	${}^2B_{1g} \rightarrow {}^2E_g$

λ = wave length in nanometers, Abs = Absorbance

III. H-NMR Spectrum

The $^1\text{H-NMR}$ spectrum of ligand (FHDTCP), DMSO- d_6 as a solvent is shown the following as figure (1):

Data: 0.9 ppm (S, 3H, $-\text{CH}_3$), 1.5 ppm (S, 3H, $-\text{CH}_3$), 1.8 ppm (S, 3H, $-\text{CH}_3$), 1.9 ppm (d, 2H, $-\text{CH}_2-$), 2.1 ppm (q, 2H, $-\text{CH}_2-$), 2.2 ppm (t, 2H, $-\text{CH}_2-$), 2.3 ppm (t, 2H, $-\text{CH}_2-$), 4.1 ppm (S, 2H, $-\text{CH}_2-$), 1.4 ppm (q, 1H, $-\text{CH}$), 1.7 ppm (q, 1H, $-\text{CH}$), 1.85 ppm (t, 1H, $-\text{CH}$), 4 ppm (S, 1H, $-\text{CH}$), 5.1 ppm (S, 1H, $-\text{OH}$), 5.8 ppm (S, 1H, $-\text{OH}$), 6 ppm (S, 1H, $-\text{OH}$), 6.4 ppm (S, 2H, $-\text{NH}_2$), 6.2 ppm (S, 1H, $-\text{C}=\text{CH}$), 6.5 ppm (S, 1H, $\text{HC}=\text{C}-$), and 6.7 ppm (S, 1H, $-\text{C}=\text{CH}$).

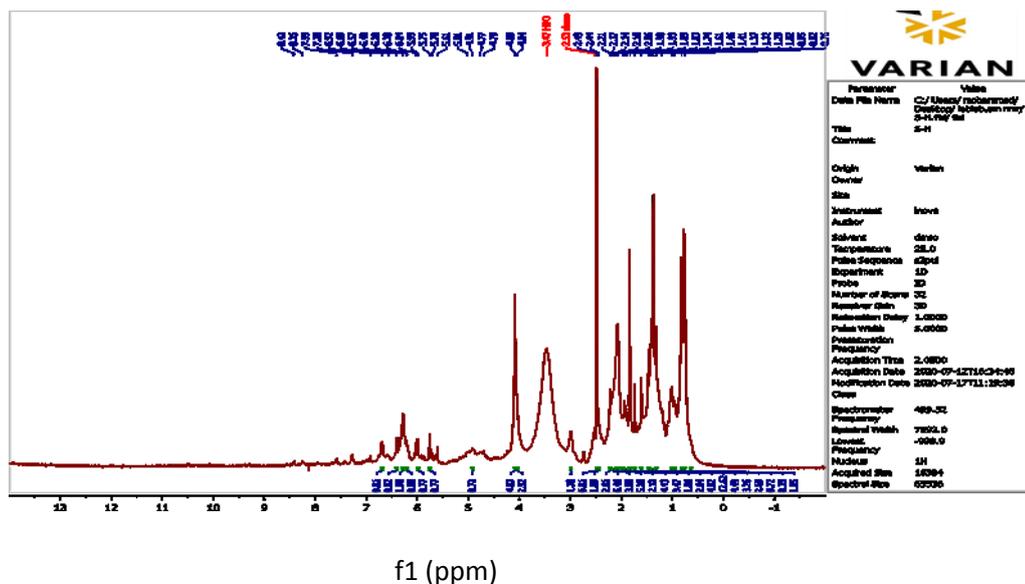


Figure 1: Measurement H-NMR to ligand (FHDTCP)

5. CONCLUSIONS

Our work shows the synthesis of new complexes with metal by the reaction salts of the metal (where $M = \text{Mn}^{+2}$, Fe^{+2} , Co^{+2} , Ni^{+2} , and Cu^{+2}) and $L = 9$ -fluoro-17-(1-hydrazono-2-hydroxyethyl)-11,17-dihydroxy-10, 13, 16-trimethyl-6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17-dodecahydro-3H cyclopenta $[\alpha]$ phenanthren-3-one (FHDTCP) as a ligand. The characterize of these new complexes by using various spectroscopic methods (UV-Visible and FT-IR), the ligand to metal mole ratio, atomic absorption and molar conductance studies and the complexities can later be studied from a biological point of view, such as measures of biological and pharmacological effectiveness, whether it can be used as an antibiotic against cancer cells or emerging viruses such as covid-19.

References

- [1] F.C. Brownfoot, C.A. Crowther, P. Middleton, "Dexamethasone see Prednisone/Dexamethasone," British Journal of Clinical Pharmacology, 30 (305), 5-16, 1990.
- [2] P.L. Havens, K.J. Wendel Berger, G.M. Hoffman, M. B. Lee, and M. J. Chasid, "Corticosteroids as Adjunctive Therapy in Bacterial Meningitis: A Meta-Analysis of Clinical Trials," American Journal of Diseases of Children, 143(9), 1051-1055, 1989.
- [3] N. Zhu, D. Zhang, and W. Wang, "A Novel Coronavirus from Patients with Pneumonia in China," The new England Journal of Medicine, 382(4), 727-733, 2019.
- [4] W. Choi, I. N. Houpis, A. Molina, J.E. Lynch, R. P. Volante, P.J. Reider and A.O. King, "Taking Stock of Maternal, Newborn, and Child Survival," British Journal Clinical Pharmacology, 36(4), 4571, 1995.
- [5] C. M. Oddo, "Intraneural Stimulation Elicits Discrimination of Textural Features by Artificial Fingertip in Intact and Amputee Humans," Jundishapur Scientific Medical Journal, 5(3), 213-222, 2016.

- [6] U. Baschant, and J. Tuckermann, "The Role of the Glucocorticoid Receptor in Inflammation and Immunity," *Journal of Steroid Biochemistry*, 1(12), 69-75, 2010.
- [7] J. K. Son, L.X. Zhao, A. Basnet, P. Thapa, R. Karki, and Y. Jahng, "Antenatal Corticosteroid Therapy for Fetal Maturation," *European Journal of Medicinal Chemistry*, 43(6), 675-682, 2008.
- [8] M. Ciriaco, P. Ventrice, G. Russo, M. Scicchitano, G. Mazzitello, F. Scicchitano, and E. Russo "Corticosteroid-Related Central Nervous System Side Effects," *Journal of Pharmacology Pharmacotherapeutics*, 15 (9), 654-668, 2013.
- [9] S. Diederich, B. Hanke, P. Burkhardt, M. Muller, M. Schoneshofer, V. Bahr and W. Oelkers, "Metabolism of Synthetic Corticosteroids by 11 Beta-Hydroxysteroid-Dehydrogenases in Man Steroids," *European Journal of Medicinal Chemistry*, 63(6), 398-412, 1998.
- [10] P. M. Kistler, J. M. Kalman, S. P. Fynn, S. Singarayar, K. C. Roberts-Thomson, C. B. Lindsay, U. Khong, P. B. Sparks, N. Strathmore, and H. G. Mond, "Rapid Decline in Acute Stimulation Thresholds with Steroid-Eluting Active-Fixation Pacing Leads," *Pace-Pacing and Clinical Electrophysiology*, 28(9), 903-909, 2005.
- [11] S. M. Spoorenberg, V. H. Deneer, J. C. Grutters, A. E. Pulles, G. P. Voorn, G. T. Rijkers, and W. J. Bos, "Pharmacokinetics of Oral vs. Intravenous Dexamethasone in Patients Hospitalized with Community-Acquired Pneumonia," *British Journal Clinical Pharmacology*, 78(1), 78-83, 2014.
- [12] R. V. Singh, M. K. Biyala, and N. Fahmi." Phosphorus, Sulfur and Silicon and the Related Elements". *American Journal of Diseases of Children*, 180 (2), 425-434, 2005.
- [13] S. Mukhopadhyay, J. R. Hoidal, and T. K. Mukherjee, "Role of TNF-Alpha in Pulmonary Pathophysiology," *Respiratory Research*, 7(1),125, 2006.
- [14] E. S. Tomlinson, J. L. Maggs, B. K. Park, and D. J. Back, "Dexamethasone Metabolism in Vitro: Species Differences," *Journal of Steroid Biochemistry Molecular Biology*, 62 (4), 345-52, 1997.
- [15] A. Mahasin, K. Huda, and S. Carolin, " Drug Discovery and Medicinal Chemistry for Psychiatric Disorders," *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 15(5), 28-34, 2014.
- [16] E. Yousif, A. Majeed, K. Al-Sammarae, N. Salih, J. Salimon, and B. Abdullah, "Corticosteroids for Acute Bacteria Meningitis," *Arabian Journal of Chemistry*, 10(2), S1639-S1644, 2017.
- [17] F. Nayeri, K. Movaghar-Nezhad, and F. Assar-Zadegan, "Effects of Antenatal Steroids on the Incidence and Severity of Respiratory Distress Syndrome in an Iranian Hospital," *Eastern Mediterranean Health Journal*, 11(7), 716-722, 2005.
- [18] K. H. Yeh, C. C. Wang, M. S. Wen, C. C. Chou, S. J. Yeh, and D. L. Wu, "Long-Term Performance of Transvenous, Steroid-Eluting, High Impedance, Passive-Fixation Ventricular Pacing Leads," *Pace-Pacing and Clinical Electrophysiology*, 27 (10), 1399-1404, 2004.
- [19] E. B. Fortescue, C. I. Berul, F. Cecchin, E. P. Walsh, J. K. Triedman, and M. E. Alexander, "Comparison of Modern Steroid-Eluting Epicardial and thin Transvenous Pacemaker Leads in Pediatric and Congenital Heart Disease Patients," *Journal of Interventional Cardiac Electrophysiology*, 14(1), 27-36, 2005.
- [20] J. Liu, Z. C. Feng, and Q. Wang "Antenatal Dexamethasone has no Adverse Effects on Child Physical and Cognitive Development: a Long-Term Cohort Follow-up Investigation," *Journal of Maternal-Fetal and Neonatal Medicine*, 25(11), 2369-2371 2012.