chemistry proceedings

MDPI

Proceeding Paper

Calculations of Thermodynamic Parameters of Nano Cobalt Chloride with Organic Ligands Derived from 4,6-Diacetyl Resorcinol Using Conductometric Measurements †

Shorouk S. Zyn Elabeden, Sahar A. El-Molla *, Magdy Shebl, Sameh G. Sanad and Mona A. Naghmash

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt; shorouksho96@gmail.com (S.S.Z.E.); magdyshebl@edu.asu.edu.eg (M.S.); sameh_gamal010@yahoo.com (S.G.S.); monyali_88@yahoo.com (M.A.N.)

* Correspondence: saharelmolla@edu.asu.edu.eg or saharelmolla@yahoo.com

† Presented at The 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC 2024), 15–30 November 2024; Available online: https://sciforum.net/event/ecsoc-28.

Abstract: Interactions of nano cobalt chloride in the absence and presence of Schiff base ligands derived from 4,6-diacetyl resorcinol are studied thermodynamically in mixed binary solvent (DMF-H_2O). The organic ligands are nominated as EAH_2DAR and O-$PhenH_2DAR$. The nano cobalt chloride was characterized by the TEM tool. The calculated parameters depend on the conductivity of solutions measured at different temperatures and concentrations. The study was done at 298.15, 308.15, 318.15, and 328.15 K in various concentrations of a mixed solvent of dimethylformamide and water. The association parameters such as the enthalpies, entropies, free energies of association, degree of association, and association constant were calculated in the absence and presence of Schiff base ligands. The results showed the strong electrolyte behavior of nano cobalt chloride in the absence and presence of organic ligands. The interactions between cobalt species increase after adding Schiff bases ligands where the degree of dissociation decreases in the presence of ligands. Small values of degree of dissociation and s of molar conductance show that the interactions increase in the case of O-$PhenH_2DAR$ than EAH_2DAR ligand. The solution of nano cobalt chloride salt with O-$PhenH_2DAR$ has the highest values of association constants and more negative Gibbs free energies at all temperatures and concentrations used.

Keywords: Schiff base complex; association parameters; (DMF-H_2O) binary solvent ; Nano cobalt chloride;

Citation: Elabeden, S.S.Z.; El-Molla, S.A.; Shebl, M.; Sanad, S.G.; Naghmash, M.A. Calculations of Thermodynamic Parameters of Nano Cobalt Chloride with Organic Ligands Derived from 4,6-Diacetyl Resorcinol Using Conductometric Measurements. *Chem. Proc.* **2024**, *6*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: 15 November 2024

1. Introduction

Most Schiff base ligands have attracted scientists because they form complexes with high efficiency with transition metals [1–4]. It's found that Schiff base derived ligands can be used in a wide variety of processes, therefore synthetic chemists used it in many productions as the transformation of hydrocarbons by a catalyst into useful oxygenated derivatives as alcohols [5–11]. The complexation between Schiff base ligands and the metals nowadays has got a lot of interest because of their several applications such as agricultural applications as pesticidal and insecticidal, also can be used in dyeing, in the catalytic process, food industry and other environmental applications [12–15]. In fact, 4,6-diacetyl resorcinol (H_2DAR)-based symmetrical [16–20] and asymmetrical [21–23] Schiff bases have been successfully constructed. Complexes of these Schiff bases are distinguished by their fascinating chelating modes and biological uses [20–22].

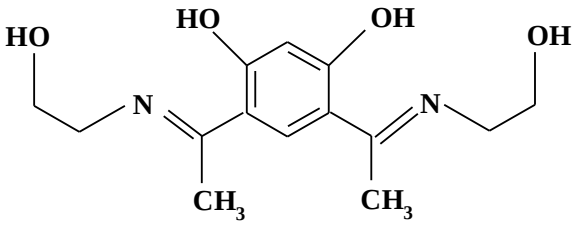
Cobalt(II) chloride has different forms according to the amounts of water it has, and the most known form is $CoCl_2.6H_2O$. The main use of cobalt(II) chloride hexahydrate is as an intermediate in the manufacture of other cobalt salts. Cobalt chloride has many usages

such as with the patients with anemia to improve hematocrit, hemoglobin, and erythrocyte values also in the preparation of catalysts, for painting on glass and porcelain, as a fertilizer additive, as a trace mineral supplement in animal feed [24,25]. Cobalt chloride ($CoCl_2$) has been used for many applications. These applications are like electrodeposited alloy to prevent corrosion and cutting tools. Cobalt chloride can be used in computer memory devices, preparation of vitamin B_{12} and for painting on glass, in addition to its usage in manufacturing other cobalt compounds [26–30].

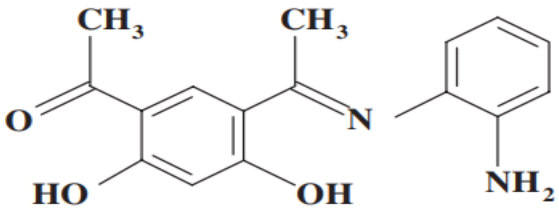
Cobalt complexes of Schiff base ligands were characterized by analytical techniques and examined for their antimicrobial activities [31–33]. In general, the transition metal complexes of Schiff base are biologically more active than the parent Schiff base [34,35].

The determination of association thermodynamic parameters has multiple usages such as to learn more about the solution. For example, the association constant calculation indicates the tendency of the salt and ligand to get together in addition to calculating the degree of dissociation that supports the results. Furthermore, determining the free energy, entropy, and enthalpies of association aids in several ways as illustrating the relationship between the system and the surrounding which therefore can be applied in chemical engineering, material science, pharmaceutical field, and others [36–40].

The aim of the work is to study thermodynamic parameters of association for nano cobalt chloride in absence and presence of polydentate Schiff bases; EAH_2DAR (Scheme 1) and O-PhenH_2DAR (Scheme 2) using conductometric measurements in DMF-H_2O mixed solvent. This study undergoes the effect of different temperatures and concentrations of DMF-water solvent to show their effect on the interaction of cobalt salt with Schiff base ligands in the solution.



Scheme 1. Structure of EAH_2DAR ligand. EAH_2DAR is the code name of the ligand; **4,6 bis(*E*)-1-(2-hydroxyethylimino)ethyl)benzene-1,3-diol.**



Scheme 2. Structure of O-PhenH_2DAR ligand. O-PhenH_2DAR is the code name of the ligand; **1-(5-(1-(2-aminophenylimino)ethyl)-2,4-dihydroxyphenyl)ethanone.**

2. Experimental

2.1. Materials

The materials used are hydrated Cobalt chloride, N,N-dimethylformamide and distilled water. Cobalt chloride and DMF are obtained from Merc company and the purity is 99.2% and 99.8%, respectively. 4,6-Diacetylresorcinol, EAH_2DAR and O-PhenH_2DAR Schiff base ligands were synthesized previously by one of the authors [19,21], respectively.

2.2. Preparation and Measurement

Different solutions of nano cobalt chloride, EAH_2DAR and O-PhenH_2DAR Schiff base ligands are prepared in (10%DMF-90%H_2O, 20%DMF-80%H_2O, 30%DMF-70%H_2O, 40%DMF-60%H_2O) separately. The concentration of salt and ligands are 1×10^{-4} M and 1×10^{-3} M respectively. The solution of each ligand was added to the cobalt (II) chloride solution individually drop by drop and measuring the conductivity each time of the mixture [42,43] The measurements were carried out for each molar ratio of the mixed solvent (water-DMF) at 298.15, 308.15, 318.15 and 328.15 K. JENCO—3173 COND conductivity bridge was used with K_{cell} equals one.

3. Results and Discussion

3.1. X-ray Diffraction

The x-ray diffraction of nano cobalt chloride is shown in Figure 1 shows peaks located at 15.82°, 17.86°, 31.55°, 33.05°, 35.01°, 37.37°, 43,57° and 48.78°, which are related to hydrated cobalt chloride. The value of the average crystal size was estimated using Scherrer equation [44]. The calculated average crystal size is 55.18 nm.

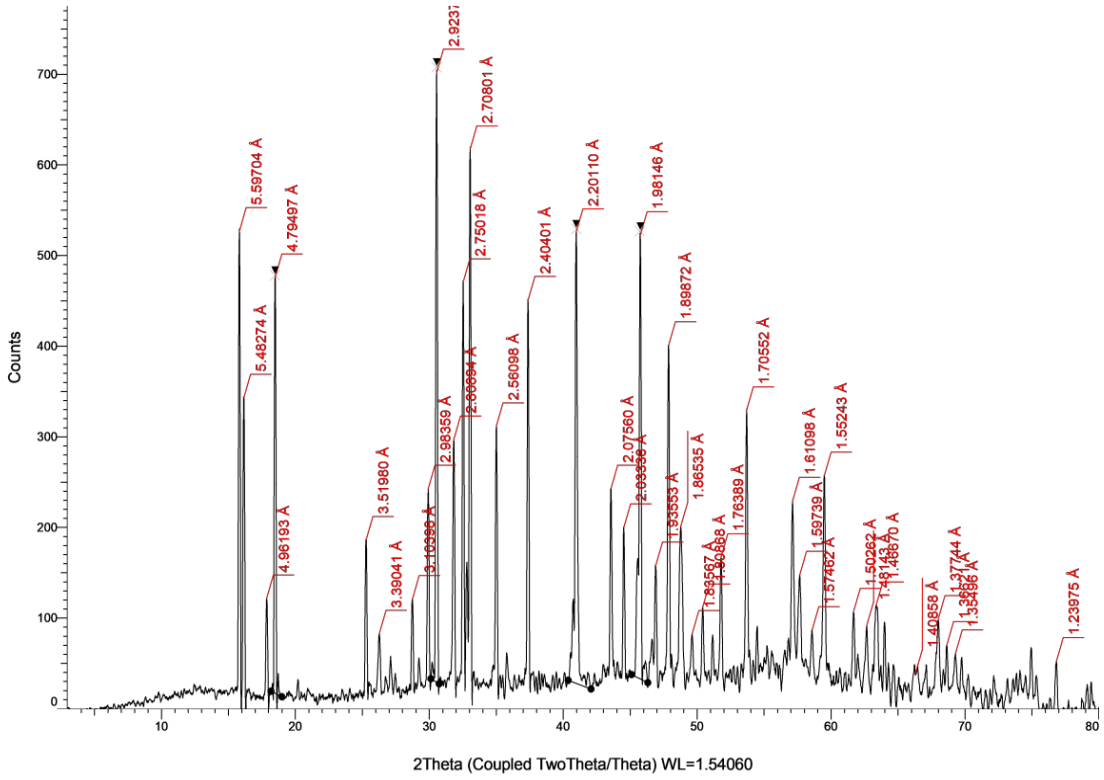


Figure 1. The X-ray diffraction of nano cobalt (II) chloride.

3.2. TEM Images

The TEM images of nano cobalt chloride in Figure 2 were obtained in ethanol by using JEOL-HRTEM-JEM2100 type (JAPAN). TEM images showed that nano cobalt chloride formed small, distorted spheres. The diameters of spheres are in the range between 6.98 nm to 9.12 nm. The obtained nano sized salts are due to the grinding using of a ball mill.

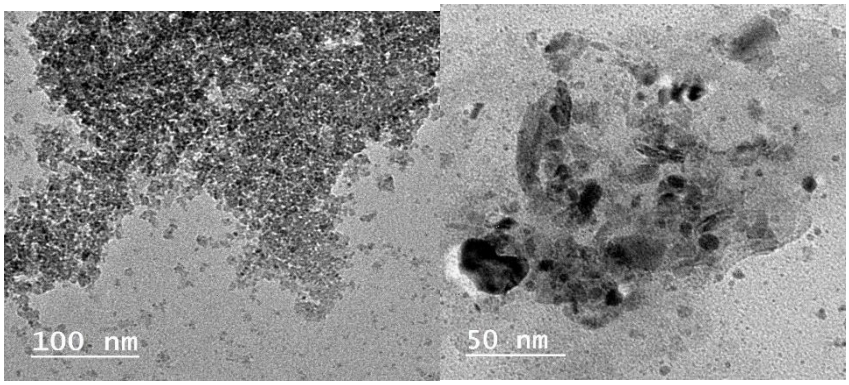


Figure 2. TEM images diffraction of nano cobalt (II) chloride.

3.3. Molar Conductance and Limiting Molar Conductance

The measurement of molar conductance and limiting molar conductance was done for nano cobalt(II) chloride in absence and presence EAH_2DAR and $O\text{-}PhenH_2DAR$ Schiff base ligands. The calculation takes place in different (*v*/*v*%) ratios of binary solvents (DMF-Water).

Molar conductance values depend on the specific conductance of solution, specific conductance of solvents and the concentration of salts were calculated by Equation (1): [45,46]

$$\Lambda_m = \frac{(K_s - K_{solv})\, K_{cell} \times 1000}{C} \quad (1)$$

where Λ_m is molar conductance, K_{solv} is specific conductance of solvent, K_s is specific conductance of solution and C is the molar conductance of the solute [47,48]

The degree of dissociation was calculated using Equation (2) [49]:

$$\alpha = \Lambda_m\, S(Z)/\Lambda_0 \quad (2)$$

where S(Z) is Fouss–Shedlovsky constant. The value of Fouss–Shedlovsky constant is equal to the unity for strong electrolytes.

Molar conductance, limiting molar conductance and degree of dissociation for nano cobalt chloride in absence and presence EAH_2DAR and $O\text{-}PhenH_2DAR$ ligands are shown in Tables 1–3, respectively.

Table 1. Molar conductance (Λ_m), limiting molar conductance (Λ_0) and degree of dissociation (α) of nano cobalt(II) chloride in the absence of ligands at different temperatures.

T(k)	Mole Fraction of DMF	Λ_m (scm² mol⁻¹)	Λ_0 (scm² mol⁻¹)	α
298.15	0.0252	1202.02	3100	0.3871
	0.0551	1000.12	2700	0.3704
	0.0909	850.32	2400	0.3542
	0.1346	804.05	2390	0.3347
308.15	0.0252	1300.13	3150	0.4127
	0.0551	1092.04	2750	0.3964
	0.0909	1005.23	2700	0.3704
	0.1346	900.41	2600	0.3462
318.15	0.0252	1550.02	3550	0.4366
	0.0551	1404.16	3350	0.4179
	0.0909	1250.38	3200	0.3906
	0.1346	1051.15	2900	0.3621
328.15	0.0252	1632.43	3550	0.4592

	0.0551	1503.06	3450	0.4348
	0.0909	1400.57	3400	0.4118
	0.1346	1202.12	3200	0.3750

Table 2. Molar conductance (Λ_m) and limiting molar conductance (Λ_0) and also degree of dissociation (α) of nano cobalt (II) chloride in the presence of EAH_2DAR ligand at different temperature.

T(k)	Mole Fraction of DMF	Λ_m (scm² mol⁻¹)	Λ_0 (scm² mol⁻¹)	α
298.15	0.0252	2350.01	8300	0.2831
	0.0551	2103.45	8000	0.2625
	0.0909	2009.72	7940	0.2519
	0.1346	905.16	4200	0.2143
308.15	0.0252	262.02	8600	0.3023
	0.0551	2300.33	8200	0.2805
	0.0909	2151.12	8150	0.2638
	0.1346	1054.03	4450	0.2360
318.15	0.0252	2703.34	8650	0.3121
	0.0551	2511.02	8500	0.2941
	0.0909	2350.52	8450	0.2781
	0.1346	1212.01	4850	0.2474
328.15	0.0252	2850.36	8900	0.3202
	0.0551	2604.15	8600	0.3023
	0.0909	2509.10	8550	0.2924
	0.1346	1502.22	5500	0.2727

Table 3. Molar conductance (Λ_m) and limiting molar conductance (Λ_0) and also degree of dissociation (α) of nano cobalt (II) chloride in the presence of $O\text{-}PhenH_2DAR$ ligand at different temperature.

T(k)	Mole Fraction of DMF	Λ_m (scm² mol⁻¹)	Λ_0 (scm² mol⁻¹)	α
298.15	0.0252	851.23	3250	0.2615
	0.0551	572.03	2400	0.2375
	0.0909	475.10	2300	0.2065
	0.1346	302.45	1650	0.1818
308.15	0.0252	950.35	3350	0.2836
	0.0551	754.01	3100	0.2419
	0.0909	581.22	2700	0.2148
	0.1346	352.14	1850	0.1892
318.15	0.0252	1041.20	3550	0.2930
	0.0551	783.55	3150	0.2476
	0.0909	660.13	2950	0.2237
	0.1346	461.72	2250	0.2044
328.15	0.0252	1122.05	3600	0.3111
	0.0551	904.33	3450	0.2609
	0.0909	691.24	3000	0.2300
	0.1346	613.09	2800	0.2179

The interactions increase after the addition of Schiff bases ligands in which the degree of dissociation decreases in presence of ligands. Small values of degree of dissociation and small values of molar conductance show that the interactions increase in case of $O\text{-}PhenH_2DAR$ than EAH_2DAR ligand.

3.4. Molar Conductance and Concentration of Cobalt Salt

The relation between molar conductance and square root of concentration of nano cobalt salt are studied in absence and presence of ligands at different temperatures 298.15, 308.15, 318.15 and 328.15 K.The relation between molar conductance and $C^{1/2}$ are shown in Figures 3–5 in which series 1: 10% DMF-90% water, series 2: 20%DMF-80% water, series 3: 30%DMF-70% water and series 4: 40% DMF-60% water. The limiting molar conductance is calculated from the extrapolation of the lines.

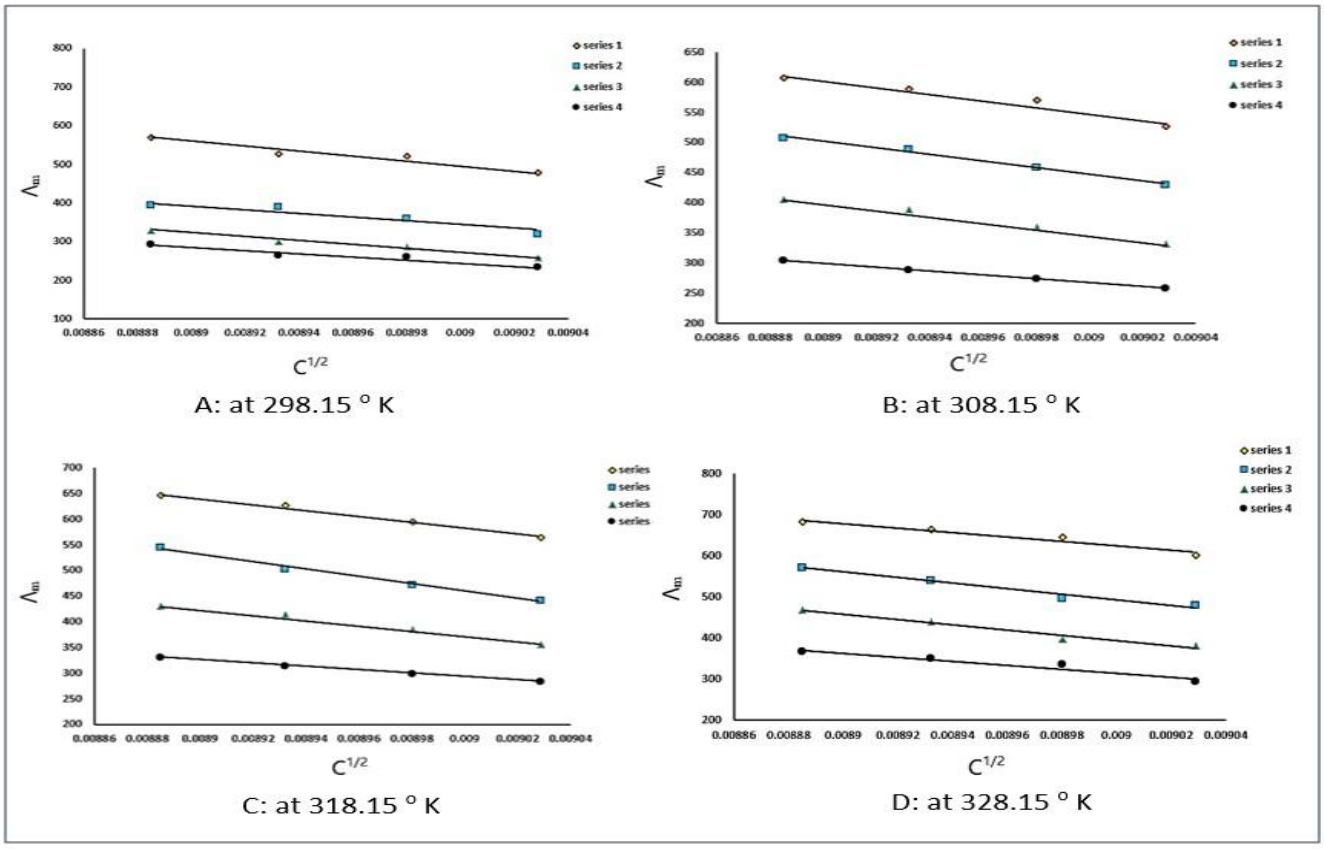


Figure 3. Relation between Λ_m and $C^{1/2}$ for nano cobalt (II) chloride in absence of ligands at different temperatures.

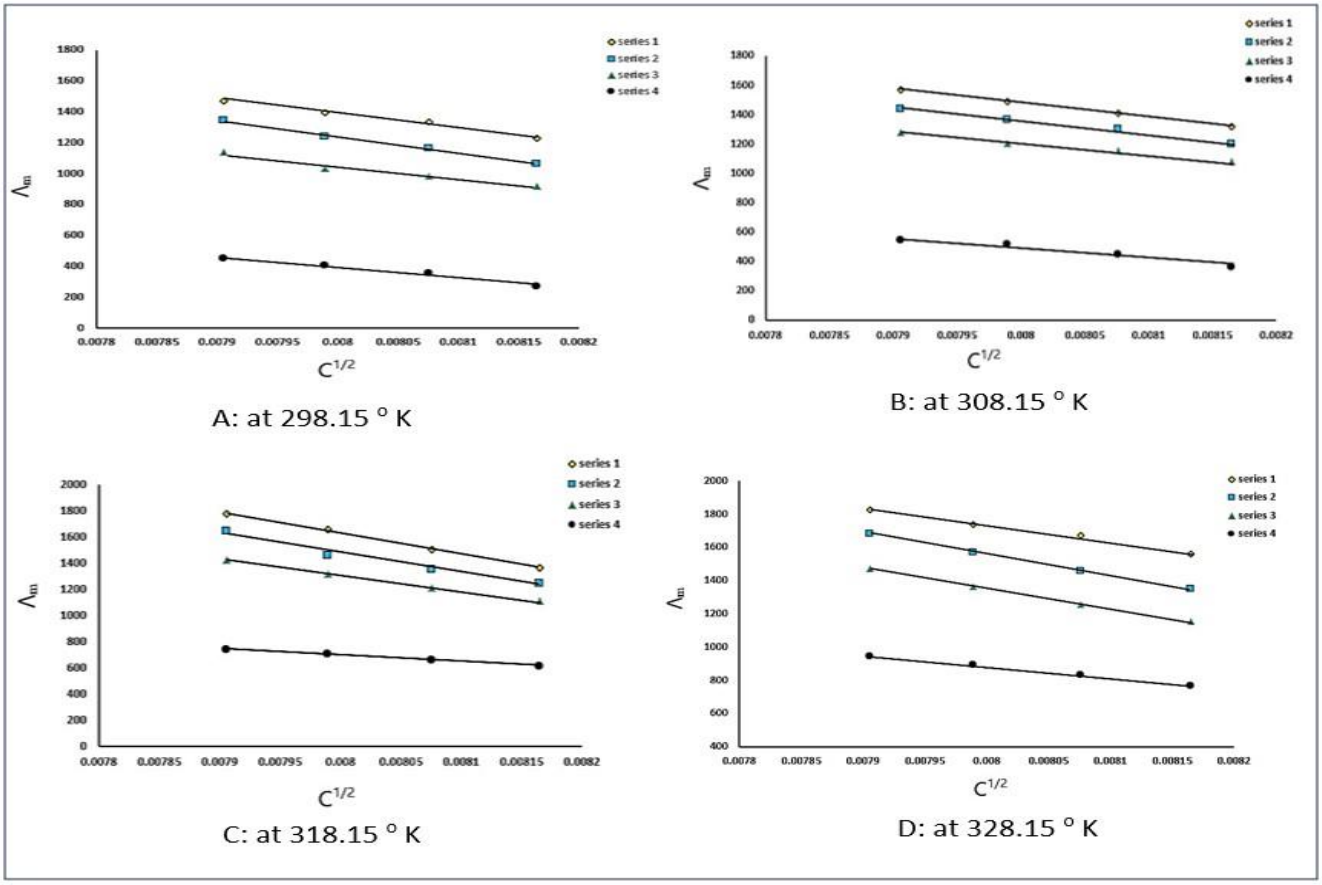


Figure 4. Relation between Λ_m and $C^{1/2}$ for nano cobalt (II) chloride in presence of EAH_2DAR at different temperatures.

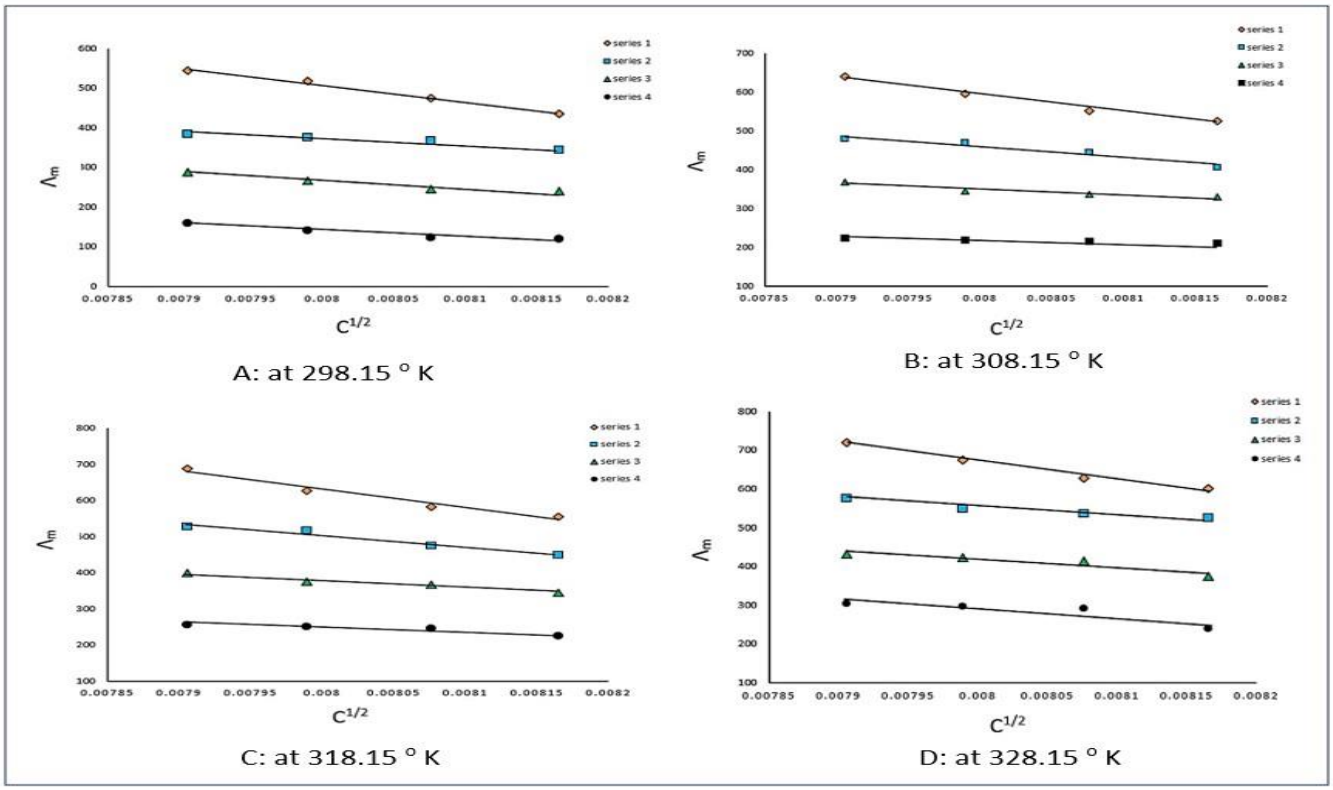


Figure 5. Relation between Λ_m and $C^{1/2}$ for nano cobalt (II) chloride in presence of O-PhenH_2DAR at different temperatures.

Straight lines were obtained at all temperatures and concentrations of mixed DMF-water solvents showing strong electrolyte behavior of nano cobalt chloride in the absence and presence of ligands.

3.5. Thermodynamic Parameters of Interactions

Thermodynamic parameters of interactions; K_A, ΔG_A, ΔH_A and ΔS_A are calculated where K_A is the association constant, ΔG_A is Gibbs free energy, ΔH_A and ΔS_A are enthalpy and entropy of interaction process respectively. Tables 5–7 show the interactions parameters values in absence and presence of EAH_2DAR and O-PhenH_2DAR with nano cobalt chloride. To calculate interaction parameters, the following equations are used [50–56]

$$K_A = \frac{\Lambda_0 (\Lambda_0 - S(Z)\, \Lambda_m)}{C_m\, \Lambda_m^2\, S(Z)^2 \gamma_{\pm}^2} \quad (3)$$

$$\Delta G_A = -R\, T \ln K_A \quad (4)$$

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (5)$$

Such that; Λ_o is limiting molar conductance, Λ_m is molar conductance, S(Z) is fousshedlovsky factor and $\gamma_{\pm}$ is the activity coefficient. ΔH_A is calculated from the slope of Figures 6 and 7 [57,58]

Table 5. Association constants (K_A), free energies of association (ΔG_A), enthalpies of association (ΔH_A) and entropies of association (ΔS_A) of nano cobalt(II) chloride in the absence of the ligands at different temperatures.

T(K)	X_S of DMF	K_A	ΔG_A (kJ mol^{-1})	ΔH_A (kJ mol^{-1})	TΔS	ΔS_A (kJ mol^{-1} K)
298.15	0.0252	6.5114×10^4	−27.4750	−12.6349	14.8401	0.0498
	0.0551	7.3069×10^4	−27.7607	−11.6342	16.1264	0.0541
	0.0909	8.1964×10^4	−28.0455	−10.7362	17.3092	0.0581
	0.1346	9.4522×10^4	−28.3988	−7.9845	20.4143	0.0685
308.15	0.0252	5.4893×10^4	−27.9590	−12.6349	15.3241	0.0497
	0.0551	6.1166×10^4	−28.2362	−11.6342	16.6020	0.0539
	0.0909	7.3069×10^4	−28.6918	−10.7362	17.9556	0.0583
	0.1346	8.6867×10^4	−29.1350	−7.9845	21.1504	0.0686
318.15	0.0252	4.7045×10^4	−28.4583	−12.6349	15.8234	0.0497
	0.0551	5.3057×10^4	−28.7764	−11.6342	17.1421	0.0539
	0.0909	6.3575×10^4	−29.2547	−10.7362	18.5185	0.0582
	0.1346	7.7466×10^4	−29.7774	−7.9845	21.7929	0.0685
328.15	0.0252	4.0839×10^4	−28.9668	−12.6349	16.3319	0.0498
	0.0551	4.7598×10^4	−29.3846	−11.6342	17.7504	0.0541
	0.0909	5.5230×10^4	−29.7903	−10.7362	19.0541	0.0581
	0.1346	7.0752×10^4	−30.4661	−7.9845	22.4815	0.0685

Table 6. Association constants (K_A), free energies of association (ΔG_A), enthalpies of association (ΔH_A) and entropies of association (ΔS_A) of nano cobalt(II) chloride in the presence of EAH_2DAR at different temperatures.

T(K)	X_S of DMF	K_A	ΔG_A (kJ mol^{-1})	ΔH_A (kJ mol^{-1})	TΔS	ΔS_A (kJ mol^{-1} K)
298.15	0.0252	1.8550×10^5	−30.0701	−7.9775	22.0926	0.0741
	0.0551	2.2202×10^5	−30.5156	−9.2090	21.3066	0.0715
	0.0909	2.4459×10^5	−30.7555	−9.6344	21.1212	0.0708
	0.1346	3.5495×10^5	−31.6787	−14.5268	17.1519	0.0575
308.15	0.0252	1.5834×10^5	−30.6731	−7.9775	22.6956	0.0737
	0.0551	1.8971×10^5	−31.1362	−9.2090	21.9272	0.0712
	0.0909	2.1944×10^5	−31.5092	−9.6344	21.8748	0.0710
	0.1346	2.8468×10^5	−32.1759	−14.5268	17.6491	0.0573
318.15	0.0252	1.4645×10^5	−31.4620	−7.9775	23.4846	0.0738
	0.0551	1.6927×10^5	−31.8450	−9.2090	22.6361	0.0711
	0.0909	1.9362×10^5	−32.2005	−9.6344	22.5661	0.0709
	0.1346	2.5501×10^5	−32.9290	−14.5268	18.4022	0.0578
328.15	0.0252	1.3751×10^5	−32.2791	−7.9775	24.3016	0.0741
	0.0551	1.5834×10^5	−32.6639	−9.2090	23.4549	0.0715
	0.0909	1.7168×10^5	−32.8846	−9.6344	23.2502	0.0709
	0.1346	2.0283×10^5	−33.3394	−14.5268	18.8126	0.0573

Table 7. Association constants (K_A), free energies of association (ΔG_A), enthalpies of association (ΔH_A) and entropies of association (ΔS_A) of nano cobalt(II) chloride in the presence of $O\text{-}PhenH_2DAR$ at different temperatures.

T(K)	X_S of DMF	K_A	ΔG_A (kJ mol^{-1})	ΔH_A (kJ mol^{-1})	TΔS	ΔS_A (kJ mol^{-1} K)
298.15	0.0252	2.2395×10^5	−30.5370	−6.3774	24.1596	0.0810
	0.0551	2.8042×10^5	−31.0944	−7.3913	23.7031	0.0795
	0.0909	3.8592×10^5	−31.8860	−7.5601	24.3259	0.0816
	0.1346	5.1341×10^5	−32.5936	−14.1927	18.4009	0.0617
308.15	0.0252	1.8480×10^5	−31.0689	−6.3774	24.6915	0.0801
	0.0551	2.6866×10^5	−32.0275	−7.3913	24.6363	0.0799
	0.0909	3.5297×10^5	−32.7268	−7.5601	25.1667	0.0817
	0.1346	4.6991×10^5	−33.4600	−14.1927	19.2672	0.0625
318.15	0.0252	1.7089×10^5	−31.8703	−6.3774	25.4929	0.0801
	0.0551	2.5454×10^5	−32.9241	−7.3913	25.5329	0.0803
	0.0909	3.2171×10^5	−33.5435	−7.5601	25.9834	0.0817
	0.1346	3.9483×10^5	−34.0853	−14.1927	19.8926	0.0625
328.15	0.0252	1.4764×10^5	−32.4730	−6.3774	26.0956	0.0795
	0.0551	2.2530×10^5	−33.6261	−7.3913	26.2348	0.0799
	0.0909	3.0194×10^5	−34.4249	−7.5601	26.8648	0.0819
	0.1346	3.4185×10^5	−34.7636	−14.1927	20.5708	0.0627

The values of association constant and free energies enthalpies prove again the interactions increase in presence of ligands especially $O\text{-}PhenH_2DAR$. The solution of nano cobalt chloride salt with $O\text{-}PhenH_2DAR$ has the highest values of association constants and more negative Gibbs free energies at all temperatures and concentrations used.

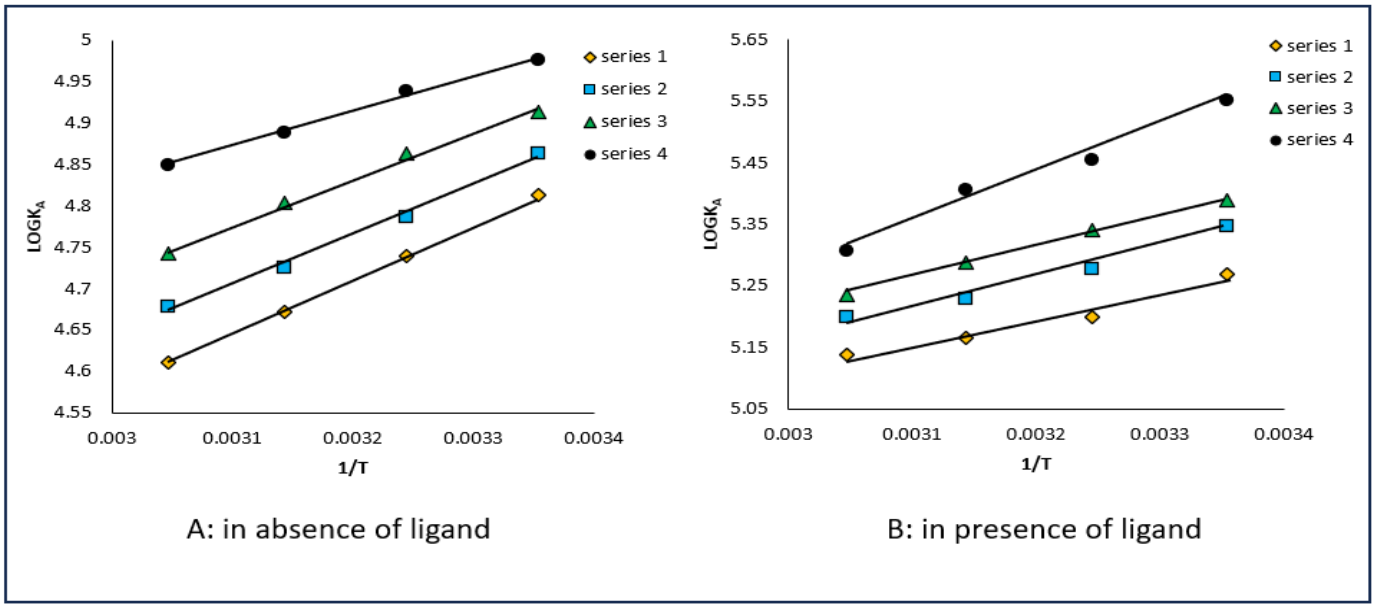


Figure 6. Relation between log K_A and 1/T for nano cobalt(II) chloride in absence and presence of EAH_2DAR ligand. Series 1: 10% DMF-90% water; Series 2: 20% DMF-80% water; Series 3: 30% DMF-70% water; Series 4: 40% DMF-60% water.

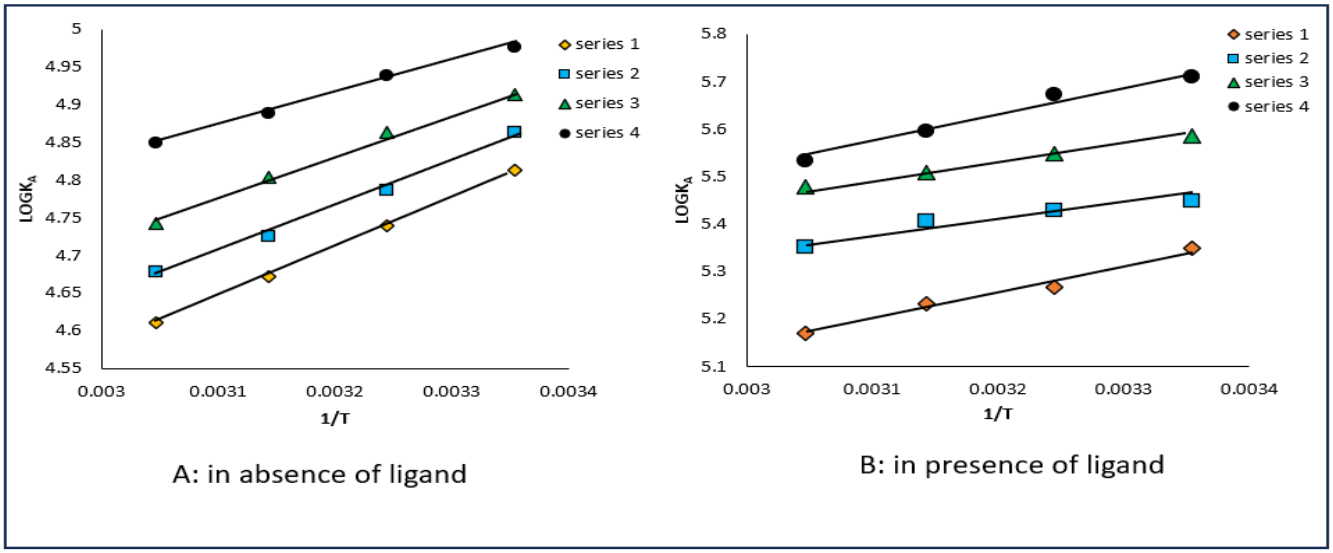


Figure 7. Relation between log K_A and 1/T for nano cobalt(II) chloride in absence and presence of O-$PhenH_2DAR$ ligand. Series 1: 10% DMF-90% water; Series 2: 20% DMF-80% water; Series 3: 30% DMF-70% water; Series 4: 40% DMF-60% water.

3.6. Relation Between Log K_A and 1/T

The relation between logarithm of association constant and 1/temperature before and after addition of each ligand are shown in Figures 6 and 7.

Directly relation between log K_A and 1/T means negative enthalpies which mean that the interaction process in absence and presence of ligand is exothermic process.

4. Conclusions

The behavior of the salt towards the association process increases after the addition of ligands according to the following trend: Association of salt alone < association of salt with EAH_2DAR < association of salt with O-$PhenH_2DAR$. Different thermodynamic

parameters indicate that the interactions in presence of O-PhenH_2DAR are the highest and this agreement with the steric effect of O-PhenH_2DAR structure. These parameters are small values of molar conductance, small values of degree of dissociation, more negative free energies and highest association constants.

Author Contributions:

Funding:

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement:

Conflicts of Interest:

References

1. Yadav, M.; Sharma, S.; Devi, J. Designing, spectroscopic characterization, biological screening and antioxidant activity of mononuclear transition metal complexes of bidentate Schiff base hydrazones. *J. Chem. Sci.* **2021**, *133*, 21.
2. Singh, A.; Gogoi, H.P.; Barman, P.; Guha, A.K. Novel thioether Schiff base transition metal complexes: Design, synthesis, characterization, molecular docking, computational, biological and catalytic studies. *Appl. Organomet. Chem.* **2022**, *36*, 66–73.
3. Dhingra, N.; Singh, J.; Singh, H.L. Synthesis, spectroscopy, and density functional theory of organotin and organosilicon complexes of bioactive ligands containing nitrogen, sulfur donor atoms as antimicrobial agents: In vitro and in silico studies. *Dalton Trans.* **2022**, *51*, 8821–8831.
4. Iacopetta, D.; Ceramella, J.; Catalano, A.; Mariconda, A.; Giuzio, F.; Saturnino, C.; Longo, P.; Sinicropi, M.S. Metal Complexes with Schiff Bases as Antimicrobials and Catalysts. *Inorganics* **2023**, *11*, 320.
5. Upendranath, K.; Venkatesh, T.; Nayaka, Y.A.; Shashank, M.; Nagaraju, G. *Inorg. Chem. Commun.* **2022**, *139*, 109354.
6. Satheesh, C.E.; Sathish Kumar, P.N.; Kumara, P.R.; Karvembu, R.; Hosamani, A.; Nethaji, M. *Appl. Organomet. Chem.* **2019**, *33*, e5111.
7. Sundar, N.; Srinivasan, A.K.; Keerthana, P.; Johan Stanley, S.; Ananda Kumar, G. Schiff's base (SB) modified zirconium dioxide reinforced PLA bio-composite film for industrial packaging applications. *Compos. Commun.* **2021**, *25*, 100750.
8. Singh, S. Synthesis, spectroscopic studies and pesticidal activity of transition metal complexes with unsymmetrical schiff base. *Indian J. Biochem. Biophys.* **2021**, *58*, 565–571.
9. Natesan, S.; Samuel, J.S.; Srinivasan, A.K. Design and development of Schiff's base (SB)-modified polylactic acid (PLA) antimicrobial film for packaging applications. *Polym. Bull.* **2022**, *79*, 4627–4646.
10. Fakhari, A.R.; Khorrami, A.R.; Naeimi, H. Synthesis and analytical application of a novel tetradentate N_2O_2 Schiff base as a chromogenic reagent for determination of nickel in some natural food samples. *Talanta* **2005**, *66*, 813.
11. Kapoor, P.; Singh, R.V.; Fahmi, N. Coordination chemistry of rare earth metal complexes with coumarin-based imines: Eco-friendly synthesis, characterization, antimicrobial, DNA cleavage, pesticidal, and nematicidal activity evaluations. *J. Coord. Chem.* **2012**, *65*, 262–277.
12. Ali, A.E. Synthesis, spectral, thermal and antimicrobial studies of some new tri metallic biologically active ceftriaxone complexes. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2011**, *78*, 224–230.
13. Karmakar, I.; Mandal, S.; Mitra, A. Evaluation of antimicrobial and insect repellent properties of two novel Zinc (II), and Nickel(II) complexes containing a tetradentate Schiff Base. *J. Integr. Sci. Technol.* **2015**, *3*, 60–67.
14. Oiye, N.; Ribeiro, M.F.M.; Katayama, J.M.T.; Tadini, M.C.; Balbino, M.A.; Eleotério, I.C.; Magalhães, J.; Castro, A.S.; Silva, R.S.M.; Júnior, J.W.d.C.; et al. Electrochemical Sensors Containing Schiff Bases and their Transition Metal Complexes to Detect Analytes of Forensic, Pharmaceutical and Environmental Interest. A Review. *Crit. Rev. Anal. Chem.* **2019**, *49*, 488–509.
15. Wei, W.; Liu, Z.; Liang, C.; Han, G.-C.; Han, J.; Zhang, S. Synthesis, characterization and corrosion inhibition behavior of 2-aminofluorene bis-Schiff bases in circulating cooling water. *RSC Adv.* **2020**, *10*, 17816–17828.
16. Kulkarni, N.V.; Sathisha, M.; Budagumpi, S.; Kurdekar, G.S.; Revankar, V.K. Binuclear transition metal complexes of bicompartmental SNO donor ligands: Synthesis, characterization, and electrochemistry. *J. Co-ord. Chem.* **2010**, *63*, 1451–1461.
17. Slassi, S.; Aarjane, M.; Amine, A. Synthesis, spectroscopic characterization (FT-IR, NMR, UV-Vis), DFT study, antibacterial and antioxidant in vitro investigations of 4,6-bis((E)-1-((3-(1H-imidazol-1-yl)propyl)imino)ethyl)benzene-1,3-diol. *J. Mol. Struct.* **2022**, *1255*, 132457.
18. Shebl, M. Synthesis and spectroscopic studies of binuclear metal complexes of a tetradentate N2O2 Schiff base ligand derived from 4,6-diacetylresorcinol and benzylamine. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2008**, *70*, 850–859.
19. Shebl, M. Synthesis, spectral and magnetic studies of mono- and bi-nuclear metal complexes of a new bis(tridentate NO2) Schiff base ligand derived from 4,6-diacetylresorcinol and ethanolamine. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2009**, *73*, 313–323.

20. Al-Harbi, S.A.; Bashandy, M.S.; Al-Saidi, H.M.; Emara, A.A.; Mousa, T.A. Synthesis, spectroscopic properties, molecular docking, anti-colon cancer and anti-microbial studies of some novel metal complexes for 2-amino-4-phenylthiazole derivative. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2015**, *145*, 425–439.
21. Shebl, M. Mononuclear, homo- and hetero-binuclear complexes of 1-(5-(1-(2-aminophenylimino)ethyl)-2,4-dihydroxyphenyl)ethanone: Synthesis, magnetic, spectral, antimicrobial, antioxidant, and antitumor studies. *J. Coord. Chem.* **2016**, *69*, 199–214.
22. Mahmoud, W.H.; Omar, M.; Ahmed, Y.M.; Mohamed, G.G. Transition metal complexes of Schiff base ligand based on 4,6-diacetyl resorcinol. *Appl. Organomet. Chem.* **2020**, *34*, e5528.
23. Ahmed, Y.M.; Mahmoud, W.H.; Omar, M.M.; Mohamed, G.G. Synthesis, Characterization and Biological Activity of Transition Metals Schiff Base Complexes Derived from 4,6-Diacetylresorcinol and 1,8-Naphthalenediamine. *J. Inorg. Organomet. Polym. Mater.* **2021**, *31*, 2339–2359.
24. Anacona, J.R.; Patiño, C. Metalloantibiotics: Synthesis and antibacterial activity of ceftazidime metal complexes. *J. Co-ord. Chem.* **2009**, *62*, 613–621.
25. Chohan, Z.H.; Supuran, C.T. *In-vitro*antibacterial and cytotoxic activity of cobalt (ii), copper (ii), nickel (ii) and zinc (ii) complexes of the antibiotic drug cephalothin (Keflin). *J. Enzym. Inhib. Med. Chem.* **2005**, *20*, 463–468.
26. Osman, D.; Cooke, A.; Young, T.R.; Deery, E.; Robinson, N.J.; Warren, M.J. The requirement for cobalt in vitamin B12: A paradigm for protein metalation. *Biochim. Et Biophys. Acta (BBA) Mol. Cell Res.* **2021**, *1868*, 118896.
27. Kongstein, O.E.; Haarberg, G.M.; Thonstad, J. Mass Transfer of Protons during Electrodeposition of Cobalt in Chloride Electrolytes. *J. Electrochem. Soc.* **2010**, *157*, D335–D340.
28. Ahmed, R.; Ibrahiem, A.A.; El-Sayd, E.A. Effect of Cobalt Chloride on the Optical Properties of PVA/PEG Blend. *Arab. J. Nucl. Sci. Appl.* **2019**, *52*, 22–32.
29. Majhi, M.; Choudhary, R.B.; Maji, P. CoCl2 reinforced polymeric nanocomposites of conjugated polymer (polyaniline) and its conductive properties. *Bull. Mater. Sci.* **2015**, *38*, 1195–1203.
30. Ahmed, R.M. Optical Properties and Structure of Cobalt Chloride Doped PVA and Its Blend with PVP. *Int. J. Mod. Phys. B* **2014**, *28*, 1450036.
31. Garnovskii, A.D.; Nivorozhkin, A.L.; Minkin, V.I. Ligand environment and the structure of schiff base adducts and tetracoordinated metal-chelates. *Co-ord. Chem. Rev.* **1993**, *126*, 1–69.
32. Raman, N.; Joseph, J.; Sakthivel, A.; Jeyamurugan, R. Synthesis, Structural Characterization and Antimicrobial Studies of Novel Schiff Base Copper(II) Complexes. *J. Chil. Chem. Soc.* **2009**, *54*, 354–357.
33. Sultana, N.; Arayne, M.S.; Afzal, M. Synthesis and antibacterial activity of cephradine metal complexes : Part II complexes with cobalt, copper, zinc and cadmium. *J. Pharm. Sci.* **2005**, *18*, 36–42.
34. El-Shahawi, M.; Al-Jahdali, M.; Bashammakh, A.; Al-Sibaai, A.; Nassef, H. Spectroscopic and electrochemical characterization of some Schiff base metal complexes containing benzoin moiety. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2013**, *113*, 459–465.
35. Offiong, O.E. Synthesis and spectral studies of platinum metal complexes of benzoin thiosemicarbazone. *Spectrochim. Acta Part A Mol. Spectrosc.* **1994**, *50*, 2167–2175.
36. AbouElleef, E.M.; Mekkey, S.D. Study of the Thermodynamic Parameters for Interaction of Ciprofloxacin Antibiotic with Bulk and Nanocopper Sulfate. *J. Biochem. Technol.* **2019**, *10*, 57–66.
37. Ben-Amotz, D.; Honig, J.M. Rectification of thermodynamic inequalities. *J. Chem. Phys.* **2003**, *118*, 5932–5936.
38. DeVoe, H. A Comparison of Local and Global Formulations of Thermodynamics. *J. Chem. Educ.* **2013**, *90*, 591–597.
39. El-Hady, M.N.A.; Zaky, R.R.; Ibrahim, K.M.; Gomaa, E.A. (E)-3-(2-(furan-ylmethylene)hydrazinyl)-3-oxo-N-(thiazol-2yl)propanamide complexes: Synthesis, characterization and antimicrobial studies. *J. Mol. Struct.* **2012**, *1016*, 169–180.
40. Bertrand, G.L. Thermodynamic Calculation of Work for Some Irreversible Processes. *J. Chem. Educ.* **2005**, *82*, 874–877.
41. Gomaa, E.A.; Negm, A.; Tahoon, M.A. Conductometric and volumetric study of copper sulphate in aqueous ethanol solutions at different temperatures. *J. Taibah Univ. Sci.* **2017**, *11*, 741–748.
42. Hamed, M.N.H.; Gomaa, E.A.; Sanad, S.G. Thermodynamic Interaction Parameters for Bulk and Nano$CuSO_4$ with Cresol Red in Mixed DMF-H_2O Solvents ASCIT. *J. Energy* **2015**, *2*, 1–8.
43. Cullity, B.D. *Elements of X-ray Diffraction*, 2nd ed.; Addison-Wesley Publishing Company, Inc.: Boston, MA, USA, 1956.
44. Gomaa, E.A.; Elleef, E.M.A.; Moustafa, H.M.; Tahoon, M.A. Conductance Studies on Complex Formation between Nano Zinc Sulphate and Calcon Carboxylic Acid in Methanol (MeOH)—Water at Different Temperatures. *Chem. Sci. Rev. Lett.* **2014**, *3*, 836–846.
45. Gomaa, E.A.; Tahoon, M.A. Ion association and solvation behavior of copper sulfate in binary aqueous–methanol mixtures at different temperatures. *J. Mol. Liq.* **2016**, *214*, 19–23.
46. Gomaa, E.A.; Mousa, M.A.; Zaky, R.R.; Rashad, R.T. Association Thermodynamic Parameters (Conductometrically) for Nano Cobalt Sulfate in Mixed EtOH–H2O Solvents at Different Temperatures. *Ijesrt J.* **2014**, *3*, 333–343.
47. Sanad, S.G.; Shebl, M. Association thermodynamic parameters for nano $Cu(NO_3)2.2.5H_2O$ with ligands at different temperatures. *RSC Adv.* **2022**, *12*, 28902.
48. Fathi, M.; Killa, H.; Gomaa, E.A.; Salem, S.H.; Farouk, A. Different studies on the interaction of Lead nitrate salt with Orange G. *Egypt. J. Chem.* **2023**, *66*, 357–367.

49. Gomaa, E.A.; Rashad, R.T. Association Thermodynamic Parameters (Conductometrically) for Solvation of Vanadyl sulfate in (Ethanol-Water) Mixed Solvent at Different Temperatures. *Chem. Res. J.* **2018**, *3*, 102–113.
50. El-Hammamya, N.H.; Hawatya, H.A.; Kawanab, A.I.; El-Hammamyc, M.N.; Moharema, H.M. Electrical Conductivity of s-Acetylthiocholine Halides and Perchlorate in Methanol at 40 °C. *J. Chem. Pharm. Res.* **2011**, *3*, 729–733.
51. El-Hammamy, N.H.; El-Hammamy, M.N.; Kawana, A.I. Thermodynamic Studies of Ion Association of s-Acetylthiocholine Halides and Perchlorate in Methanol Solutions. *J. Mex. Chem. Soc*. **2014**, *58*, 11–15.
52. El-Hammamy, N.H.; El-Hammamy, M.N.; El-Mallah, N.M.; Kawana, A.I. Conductance of s-Acetylthiocholine Chlorides in Non-Aqueous Solvents at 25 °C. *Asian J. Chem.* **2013**, *25*, 4760–4764.
53. Bester-Rogac, M.; Hunger, J.; Stoppa, A.; Buchner, R. Molar Conductivities and Association Constants of 1-Butyl-3-methylimidazoliumChloride and 1-Butyl-3-methylimidazolium Tetrafluoroborate in Methanol and DMSO. *J. Chem. Eng.* **2010**, *55*, 1799–1803.
54. Elleef, E.M.A.; Gomaa, E.A. Thermodynamics of Ion Association in the Saturated Solution of Barium Diphenyl amine sulfonate in Ethanol-Water Mixed Solvent. *Int. J. Eng. Innov. Technol. (IJEIT)* **2013**, *3*, 309–313.
55. Marcus, Y. Solubility and solvation in mixed solvent systems. *Pure Appl. Chern*. **1990**, *62*, 2069–2076.
56. Dehury, S.K.; Talukdar, M.; Dash, U.N. Studies on ion association and solvation of multi-charged electrolytes (potassium ferricyanide and ferrocyanide) in aqueous and aqueous D-fructose mixtures at different temperatures. *J. Chem. Pharm. Res.* **2012**, *4*, 1619–1624.
57. Gomaa, E.A.; El-Leef, E.M.A.; Shalaby, K.S.; Salem, S.E. The Association, Formation Constants and Gibbs Energies of Solvation for CoCl2 Stoichiometric Complexes with (E)-1-phenyl-2-(2-(4-((E)-phenyldiazenyl))phenyl hydrazono)-2-(phenylsulfonyl)ethanone at Different Temperatures, Journal of Environments. *Phys. Chem.* **2012**, *2*, 9–17.