

# The Association, Formation Constants and Gibbs Energies of Solvation for $\text{CoCl}_2$ Stoichiometric Complexes with (E)-1-phenyl-2-(2-(4-((E)-phenyldiazenyl))phenylhydrazono)-2-(phenylsulfonyl)ethanone at Different Temperatures

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**Abstract** the association constants, formation constants and Gibbs free energies of solvation are calculated from the conductometric titration curves of  $\text{CoCl}_2$  with (E)-1-phenyl-2-(2-(4-((E)-phenyldiazenyl))phenylhydrazono)-2-(phenylsulfonyl) ethanone (L) in absolute ethanol at 293.15, 298.15, 303.15 and 308.15 K. On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines are obtained indicating the formation of 1: 2, 1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants and Gibbs free energies of these different complexes in absolute ethanol at 293.15, 298.15, 303.15 and 308.15 K follow the order:  $K_f(2:1) > K_f(1:1) > K_f(1:2)$  for (M:L); and  $\Delta G_f(2:1) > \Delta G_f(1:1) > \Delta G_f(1:2)$  for (M:L).

**Keywords** Association Constant, Formation Constant, Gibbs Free Energy of Solvation

## 1. Introduction

The long range ion-ion interactions due to columbic forces are the most important features of electrolyte in solutions. This act together with shorter – ranged forces between the solvent molecules and between the solvent molecules and ion. Electrical conductivity (EC) is a measure of solution to conduct electric current and depends on : concentration of the ions, solvent, ligand and temperature. Current is carried out by both cations and anions, but to different degree. The conductivity due to divalent cations is more impotent than that of monovalent cations, it is not true for anions. Metal cations with  $d^0$  noble gas electron configuration (alkali and alkaline earth) metal ions together with the inert molecular ions like tetraalkylammonium, -phosphonium, -arsonium, and trialkylsulfonium ions exhibit properties mainly determined by their charge and size[1]. Solvation of such cations in protic and polar solvents is due essentially to electrostatic ion-dipole and ion induced dipole interactions. Metal cations with filled d-orbitals, the  $d^{10}$  cations, exhibits partially covalent character in their interactions, their properties depend

on the charge and size and partially on their electronegativity. Cations with incomplete d- orbitals called  $d^n$ -cations. With these cations protic and polar solvent molecules are strongly bound in complexes to a central cation through p-d orbital overlap and exchange only slowly with the bulk solvent. Therefore conductivity study is valuable on using transition metal cations[2,3].

The synthesis of transition metal complexes with Schiff bases of nitrogen, oxygen and sulfur donor has stimulated interest due to their vast variety of biological activities ranging from pharmacological, antitumor, fungicide, bactericide, anti-inflammatory, and antiviral activities[4,5]. Cobalt is the active centre of coenzymes called coalmines, the most common example of which is vitamin B12. As such it is an essential trace dietary mineral for all animals. Cobalt also is an active nutrient for bacteria, algae and fungi[6,7]. The aim of this work is the evaluation of the non-covalent behaviour of  $\text{CoCl}_2$  in presence of (E) -1- phenyl -2- (2- (4-((E)-phenyldiazenyl))phenyl)hydrazono)-2-(phenylsulfonyl)ethanone (L1) in absolute ethanol solutions at 293.15, 298.15, 303.15 and 308.15 K. these non-covalent interactions can help us for analysis of salts role in bodies and environment. This work provides the biological analyst data can help him for deterring the concentration of  $\text{CoCl}_2$  in blood and different solutions.

## 2. Experimental

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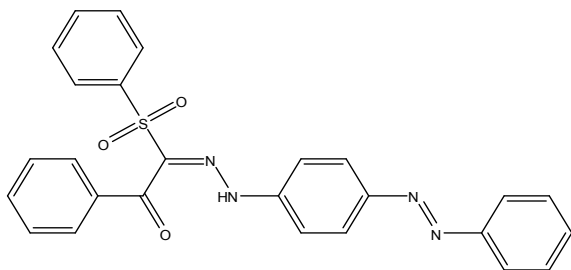
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## 2.1. Material and methods

The cobalt chloride and ethanol were provided from Merck Co.

## 2.2. The Ligand



**Scheme 1.** (E)-1-phenyl-2-(2-(4-((E)-phenyldiazenyl)phenyl)hydrazono)-2-(phenylsulfonyl)ethanone

## 2.3. Conductometric Titration

The conductometric titration of the ligand ( $1 \times 10^{-3}$ ) mole/L against  $\text{CoCl}_2$  ( $1 \times 10^{-4}$ ) mole/L in absolute ethanol was performed with 0.5 ml interval additions from  $\text{CoCl}_2$  solution. The specific conductance values were recorded using conductivity bridge HANNA, HI 8819N with a cell constant equal to 1. The conductometer was conducted with a thermostat of the type the Kottermann 4130 ultrathermostat. The temperature was adjusted at 293.15, 298.15, 303.15 and 308.15 K.

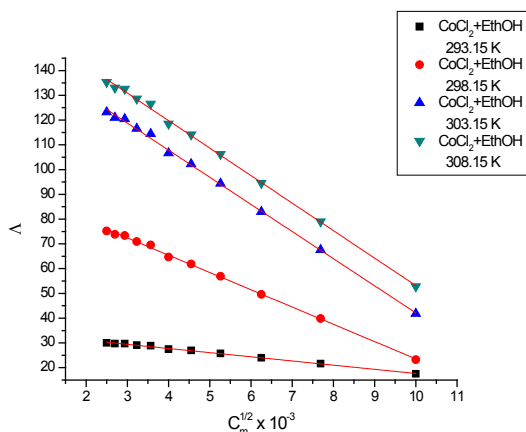
## 3. Results and Discussion

The specific conductance values ( $K_s$ ) of different concentrations of  $\text{CoCl}_2$  in absolute ethanol were measured experimentally in absence and in presence of ligand at 293.15, 298.15, 303.15 and 308.15 K.

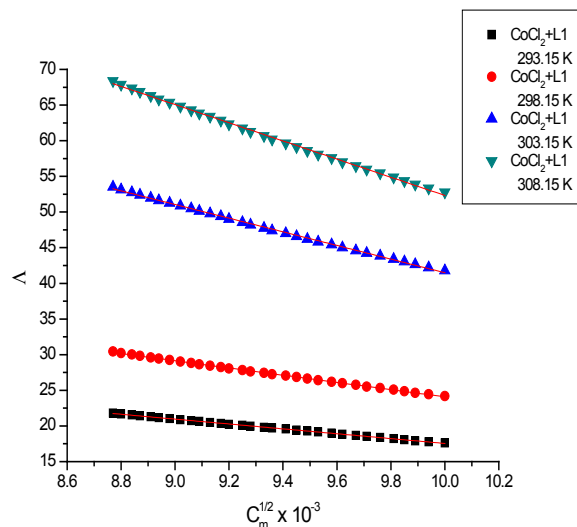
The molar conductance ( $\Lambda_m$ ) values were calculated[8] using equation

$$\Lambda_m = (K_s - K_{\text{solv}})K_{\text{cell}} \times 1000/c \quad (1)$$

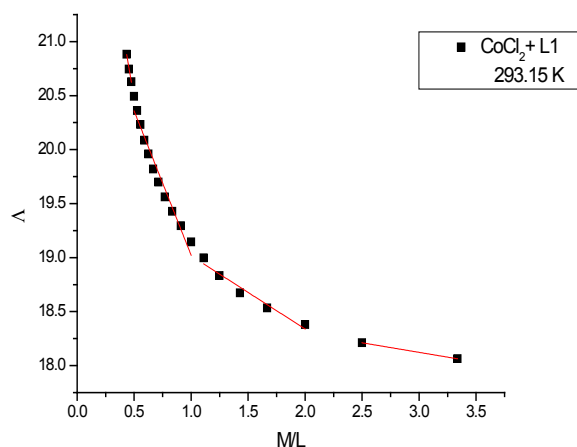
Where  $K_s$  and  $K_{\text{solv}}$  is the specific conductance of solution and the solvent, respectively;  $K_{\text{cell}}$  is the cell constant and  $C$  is the molar concentration of the  $\text{CoCl}_2$  solutions.



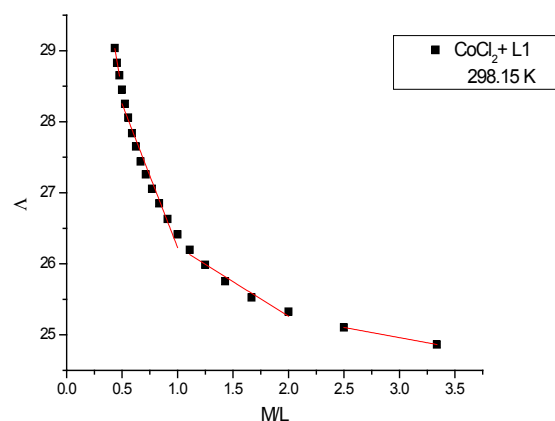
**Figure 1.** The relation between molar conductance ( $\Lambda_m$ ) and ( $\sqrt{C}$ ) of  $\text{CoCl}_2$  alone in absolute ethanol at 293.15, 298.15, 303.15 and 308.15 K



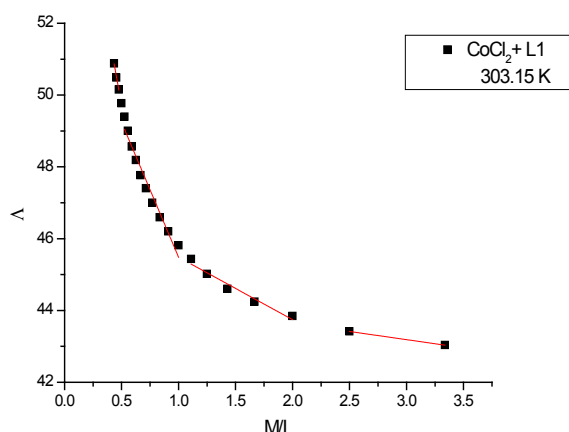
**Figure 2.** The relation between molar conductance ( $\Lambda_m$ ) and ( $\sqrt{C}$ ) of  $\text{CoCl}_2$  in the presence of ligand (L) in absolute ethanol at 293.15, 298.15, 303.15 and 308.15 K



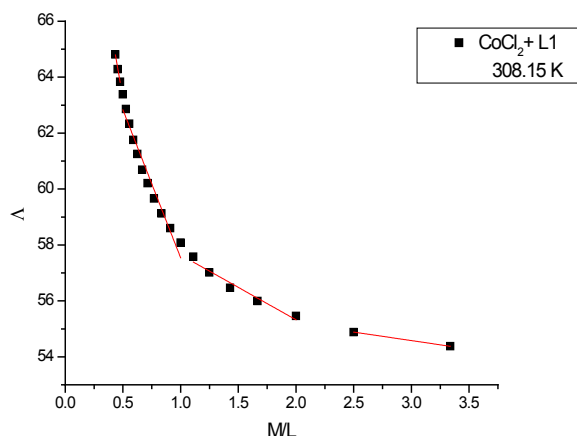
**Figure 3.** The relation between molar conductance ( $\Lambda_m$ ) and the molar ratio (M/L) of  $\text{CoCl}_2$  in presence of (L1) in absolute ethanol in 293.15 K



**Figure 4.** The relation between molar conductance ( $\Lambda_m$ ) and the molar ratio (M/L) of  $\text{CoCl}_2$  in presence of (L1) in absolute ethanol in 298.15 K



**Figure 5.** The relation between molar conductance ( $\Lambda_M$ ) and the molar ratio (M/L) of  $\text{CoCl}_2$  in presence of (L1) in absolute ethanol in 303.15 K



**Figure 6.** The relation between molar conductance ( $\Lambda_M$ ) and the molar ratio (M/L) of  $\text{CoCl}_2$  in presence of (L1) in absolute ethanol in 308.15 K

The limiting molar conductance ( $\Lambda_0$ ) at infinite dilutions were estimated for  $\text{CoCl}_2$  in absolute ethanol alone (Fig. 1) and in the presence of the ligand (L1) (Fig. 2) by extrapolating the relation between ( $\Lambda_m$ ) and  $C_m^{1/2}$  to zero concentration. By drawing the relation between molar conductance ( $\Lambda_m$ ) and the molar ratio of metal to ligand (M/L) concentrations (Fig. 3- 6), different lines are obtained with sharp breaks indicating the formation of 1:2, 1:1 and 2:1 (M : L) stoichiometric complexes. The experimental data of ( $\Lambda_m$ ) and ( $\Lambda_0$ ) were analysed for the determination of association and formation constants for each type of the stoichiometric complexes.

The association constants of  $\text{CoCl}_2$  in the presence of the ligand (L1) in absolute ethanol at 293.15, 298.15, 303.15 and 308.15 K for asymmetric electrolytes were calculated [9,10] by using equation:

$$K_A = [\Lambda_0^2 (\Lambda_0 - \Lambda_m)] / [4C_m^2 + \Lambda^3 S(z)] \quad (2)$$

Where ( $\Lambda_m$ ,  $\Lambda_0$ ) are the molar and limiting molar conductance, respectively of  $\text{CoCl}_2$ ;  $C_m$  is molar concentration of  $\text{CoCl}_2$ ,  $S(z)$  is Fuoss-Shedlovsky factor, equal with unity

for strong electrolytes [11]. The calculated association constants are shown in table 1.

The Gibbs free energies of association ( $\Delta G_A$ ) were calculated from the association constant [12,13] by applying equation :

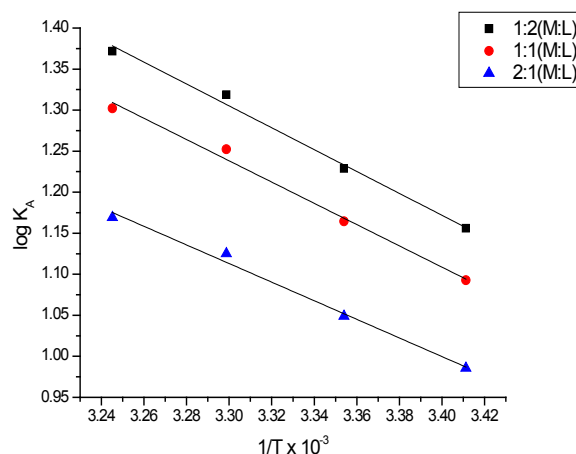
$$\Delta G_A = -RT \ln K_A \quad (3)$$

Where R is the gas constant (8.341 J) and T is the absolute temperatures (293.15, 298.15, 303.15 and 308.15 K). The calculated Gibbs free energies were presented in tables (1-4).

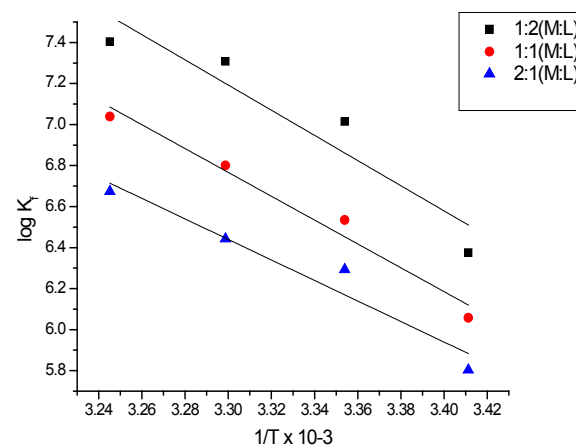
The association free energies evaluated for  $\text{CoCl}_2$  – ligand complexes are small and spontaneous indicating electrostatic attraction.

The formation constants ( $K_f$ ) for  $\text{CoCl}_2$  complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (K:L) by using equation [14,15]:

$$K_f = [\Lambda_M - \Lambda_{\text{obs}}] / [(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[L]] \quad (4)$$



**Figure 7.** The relation between  $\log(K_A)$  for (2:1), (1:1) and (1:2) stoichiometric complexes against  $1/T$



**Figure 8.** The relation between  $\log(K_f)$  for (2:1), (1:1) and (1:2) stoichiometric complexes against  $1/T$

Where  $\Lambda_m$  is the molar conductance of  $\text{CoCl}_2$  alone,  $\Lambda_{\text{obs}}$  is the molar conductance of the solution during titration and  $\Lambda_{\text{ML}}$  is the molar conductance of the complex.

**Table 1.** Association constants and Gibbs free energies of association for CoCl<sub>2</sub> with L1 in ethanol at 293.15 K

$\Lambda_{obs}$	$C_m$	$\Lambda_o - \Lambda_m$	$\Lambda_o^2(\Lambda_o - \Lambda_m)$	$4C^2 + \Lambda_m^3$	$K_A$	$\Delta G_A$
17.6	0.0001	34.0733	90980.32	5451.776	16.6882	-6.8615
17.7587	9.09E-05	33.9146	90556.49	5600.615	16.1690	-6.7845
17.9174	8.33E-05	33.7558	90132.66	5752.138	15.6694	-6.7080
18.0631	7.69E-05	33.6102	89743.76	5893.558	15.2274	-6.6382
18.2114	7.14E-05	33.4618	89347.56	6039.993	14.7926	-6.5676
18.3796	6.67E-05	33.2936	88898.58	6208.848	14.3180	-6.4881
18.5340	6.25E-05	33.1393	88486.34	6366.63	13.8984	-6.4156
18.6737	5.88E-05	32.9995	88113.24	6511.714	13.5315	-6.3504
18.8338	5.56E-05	32.8394	87685.81	6680.618	13.1254	-6.2761
18.9970	5.26E-05	32.6762	87249.99	6855.816	12.7264	-6.2008
19.1448	0.00005	32.5284	86855.34	7017.083	12.3777	-6.1331
19.2952	4.76E-05	32.3780	86453.67	7183.795	12.0345	-6.0646
19.4289	4.55E-05	32.2444	86096.89	7334.074	11.7393	-6.0040
19.5625	4.35E-05	32.1108	85740.11	7486.435	11.4527	-5.9438
19.6985	4.17E-05	31.9747	85376.81	7643.731	11.1695	-5.8827
19.8196	0.00004	31.8536	85053.46	7785.573	10.9245	-5.8287
19.9605	3.85E-05	31.7128	84677.45	7952.706	10.6476	-5.7661
20.0858	0.000037	31.5874	84342.69	8103.499	10.4081	-5.7106
20.2317	3.57E-05	31.4416	83953.33	8281.274	10.1377	-5.6465
20.3615	3.45E-05	31.3117	83606.56	8441.775	9.90390	-5.5896
20.4936	3.33E-05	31.1797	83253.97	8607.084	9.67272	-5.5320
20.6279	3.23E-05	31.0454	82895.4	8777.396	9.44419	-5.4737
20.7448	3.13E-05	30.9284	82583.18	8927.508	9.25041	-5.4232
20.8834	3.03E-05	30.7898	82213.1	9107.645	9.02682	-5.3635
21.0244	2.94E-05	30.6488	81836.59	9293.385	8.80589	-5.3031
21.1472	2.86E-05	30.5260	81508.61	9457.221	8.61866	-5.2507
21.2719	2.78E-05	30.4013	81175.68	9625.496	8.43340	-5.1977
21.4198	0.000027	30.2535	80780.87	9827.613	8.219785	-5.1352
21.5486	2.63E-05	30.1246	80436.8	10006.05	8.038817	-5.0809
21.6795	2.56E-05	29.9937	80087.41	10189.44	7.859846	-5.0260
21.8124	0.000025	29.8609	79732.58	10377.96	7.682873	-4.9705

$\Lambda_o = 51.67333$

**Table 2.** Association constants and Gibbs free energies of association for CoCl<sub>2</sub> with L1 in ethanol at 298.15K

$\Lambda_{obs}$	$C_m$	$\Lambda_o - \Lambda_m$	$\Lambda_o^2(\Lambda_o - \Lambda_m)$	$4C^2 + \Lambda_m^3$	$K_A$	$\Delta G_A$
24.2	0.0001	50.4690	281388.8	14172.49	19.8545	-7.4094
24.4444	9.09E-05	50.2246	280025.9	14606.30	19.1715	-7.3226
24.6525	8.33E-05	50.0165	278865.8	14982.47	18.6128	-7.2492
24.8644	7.69E-05	49.8045	277684.0	15372.27	18.0639	-7.1750
25.1047	7.14E-05	49.5643	276344.7	15822.14	17.4657	-7.0915
25.3252	6.67E-05	49.3438	275114.9	16242.83	16.9376	-7.0154
25.5248	6.25E-05	49.1442	274002.0	16629.94	16.4764	-6.9470
25.7535	5.88E-05	48.9155	272727.0	17080.94	15.9667	-6.8690
25.9867	5.56E-05	48.6823	271426.9	17549.12	15.4666	-6.7902
26.1978	5.26E-05	48.4711	270249.7	17980.36	15.0302	-6.7192
26.4127	0.00005	48.2563	269051.6	18426.46	14.6013	-6.6474
26.6315	4.76E-05	48.0375	267831.9	18888.08	14.1799	-6.5748
26.8502	4.55E-05	47.8188	266612.3	19357.35	13.7731	-6.5026
27.0543	4.35E-05	47.6147	265474.4	19802.12	13.4063	-6.4357
27.2584	4.17E-05	47.4106	264336.5	20253.66	13.0513	-6.3692
27.4401	0.00004	47.2289	263323.7	20661.27	12.7448	-6.3102
27.6513	3.85E-05	47.0177	262146.1	21142.07	12.3992	-6.2421
27.8393	0.000037	46.8297	261097.6	21576.36	12.1010	-6.1817
28.0581	3.57E-05	46.6109	259878.1	22088.93	11.7650	-6.1119
28.2529	3.45E-05	46.4161	258791.9	22552.23	11.4752	-6.0501
28.4509	3.33E-05	46.2180	257687.5	23029.91	11.1892	-5.9875
28.6524	3.23E-05	46.0166	256564.5	23522.52	10.9071	-5.9242
28.8278	3.13E-05	45.8412	255586.5	23957.16	10.6684	-5.8693
29.0357	3.03E-05	45.6333	254427.4	24479.23	10.3936	-5.8046
29.2472	2.94E-05	45.4218	253248.1	25018.12	10.1225	-5.7391
29.4314	2.86E-05	45.2375	252220.8	25493.90	9.8933	-5.6823
29.6185	2.78E-05	45.0505	251178.0	25983.02	9.6670	-5.6249
29.8403	0.000027	44.8287	249941.4	26571.13	9.4065	-5.5572
30.0335	2.63E-05	44.6354	248863.8	27090.79	9.1862	-5.4985
30.2298	2.56E-05	44.4392	247769.4	27625.42	8.9688	-5.4391
30.4292	0.000025	44.2398	246658.1	28175.5	8.7543	-5.3791

$\Lambda_o = 74.66907$

**Table 3.** Association constants and Gibbs free energies of association for CoCl<sub>2</sub> with L1 in ethanol at 303.15K

$\Lambda_{obs}$	$C_m$	$\Lambda_o - \Lambda_m$	$\Lambda_o^2 (\Lambda_o - \Lambda_m)$	$4C^2 + \Lambda_m^3$	$K_A$	$\Delta G_A$
41.8	0.0001	95.3782	1794810	73034.63	24.5748	-8.0714
42.2222	9.09E-05	94.9560	1786870	75270.22	23.7394	-7.9842
42.6530	8.33E-05	94.5252	1778760	77598.01	22.9228	-7.8959
43.0346	7.69E-05	94.1436	1771580	79699.08	22.2284	-7.8184
43.4161	7.14E-05	93.7621	1764400	81837.74	21.5597	-7.7414
43.8485	6.67E-05	93.3297	1756260	84307.34	20.8317	-7.6548
44.2455	6.25E-05	92.9327	1748790	86618.07	20.1897	-7.5759
44.6048	5.88E-05	92.5734	1742030	88745.42	19.6295	-7.5049
45.0164	5.56E-05	92.1617	1734280	91225.15	19.0110	-7.4242
45.4362	5.26E-05	91.7420	1726390	93800.68	18.4048	-7.3425
45.8162	0.00005	91.3620	1719230	96174.27	17.8762	-7.2691
46.2030	4.76E-05	90.9751	1711960	98630.79	17.3572	-7.1948
46.5968	4.55E-05	90.5814	1704550	101173.9	16.8477	-7.1197
46.9976	4.35E-05	90.1806	1697000	103807.5	16.3476	-7.0437
47.4058	4.17E-05	89.7724	1689320	106535.7	15.8569	-6.9669
47.7691	0.00004	89.4091	1682490	109004.0	15.4351	-6.8989
48.1915	3.85E-05	88.9866	1674540	111921.5	14.9617	-6.8204
48.5676	0.000037	88.6105	1667460	114562.5	14.5550	-6.7509
49.0051	3.57E-05	88.1731	1659230	117686.1	14.0987	-6.6706
49.3947	3.45E-05	87.7835	1651890	120515.4	13.7069	-6.5996
49.7752	3.33E-05	87.4030	1644730	123321.9	13.3369	-6.5306
50.1557	3.23E-05	87.0225	1637570	126171.7	12.9789	-6.4620
50.4870	3.13E-05	86.6912	1631340	128688.6	12.6766	-6.4026
50.8797	3.03E-05	86.2985	1623950	131714.9	12.3293	-6.3326
51.2792	2.94E-05	85.8989	1616430	134842.2	11.9876	-6.2617
51.6272	2.86E-05	85.5509	1609880	137606.2	11.6992	-6.2003
51.9805	2.78E-05	85.1977	1603240	140450.4	11.4149	-6.1383
52.3995	0.000027	84.7787	1595350	143874.0	11.0885	-6.0652
52.7646	2.63E-05	84.4136	1588480	146902.2	10.8132	-6.0018
53.1353	2.56E-05	84.0429	1581500	150020.5	10.5419	-5.9377
53.5118	0.000025	83.6663	1574423	153232.4	10.2747	-5.8730

 $\Lambda_o = 137.17826$ **Table 4.** Association constants and Gibbs free energies of association for CoCl<sub>2</sub> with L1 in ethanol at 308.15K

$\Lambda_{obs}$	$C_m$	$\Lambda_o - \Lambda_m$	$\Lambda_o^2 (\Lambda_o - \Lambda_m)$	$4C^2 + \Lambda_m^3$	$K_A$	$\Delta G_A$
52.8	0.0001	126.9446	4101341	147198	27.8627	-8.5263
53.3333	9.09E-05	126.4113	4084110	151703.7	26.9216	-8.4383
53.8775	8.33E-05	125.867	4066527	156395.2	26.0016	-8.3492
54.3769	7.69E-05	125.3677	4050393	160784.5	25.1914	-8.2681
54.8856	7.14E-05	124.8589	4033957	165339.4	24.3980	-8.1861
55.4621	6.67E-05	124.2824	4015331	170604.6	23.5358	-8.0939
55.9915	6.25E-05	123.7531	3998229	175536.2	22.7772	-8.0099
56.4705	5.88E-05	123.274	3982751	180080.6	22.1164	-7.9345
57.0194	5.56E-05	122.7252	3965019	185382.5	21.3883	-7.8487
57.5790	5.26E-05	122.1655	3946938	190894.6	20.6760	-7.7619
58.0858	0.00005	121.6588	3930566	195979.3	20.0560	-7.6839
58.6015	4.76E-05	121.1430	3913904	201246	19.4483	-7.6050
59.1265	4.55E-05	120.6181	3896942	206703.3	18.8528	-7.5253
59.6610	4.35E-05	120.0836	3879674	212359.7	18.2693	-7.4448
60.2052	4.17E-05	119.5393	3862091	218224.3	17.6978	-7.3633
60.6896	0.00004	119.0549	3846441	223534.3	17.2073	-7.2913
61.2529	3.85E-05	118.4917	3828243	229815.8	16.6578	-7.2081
61.7543	0.000037	117.9902	3812041	235506.8	16.1865	-7.1346
62.3376	3.57E-05	117.4069	3793197	242243.1	15.6586	-7.0496
62.8571	3.45E-05	116.8875	3776413	248349.8	15.2060	-6.9745
63.3853	3.33E-05	116.3592	3759348	254663.5	14.7620	-6.8985
63.8335	3.23E-05	115.9110	3744866	260104.5	14.3975	-6.8345
64.2818	3.13E-05	115.4628	3730384	265622.4	14.0439	-6.7707
64.8131	3.03E-05	114.9315	3713219	272263.2	13.6383	-6.6956
65.3536	2.94E-05	114.3909	3695755	279132.2	13.2401	-6.6197
65.8245	2.86E-05	113.9201	3680543	285208.8	12.9047	-6.5539
66.3024	2.78E-05	113.4421	3665101	291466.8	12.5746	-6.4876
66.8693	0.000027	112.8753	3646788	299006.3	12.1963	-6.4093
67.3632	2.63E-05	112.3814	3630830	305681.3	11.8778	-6.3415
67.8648	2.56E-05	111.8798	3614624	312560.6	11.5645	-6.2730
68.3742	0.000025	111.3703	3598166	319652.2	11.2565	-6.2038

 $\Lambda_o = 179.74459$

**Table 5.** Formation constants and Gibbs free energies of formation for 1:2 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 293.15 K

$\Lambda_{obs}(cm^2.Ohm^{-1})$	[L]	$(\Lambda_{obs} - \Lambda_{ML})[L]$	$(\Lambda_M - \Lambda_{obs})$	$K_f$	$\Delta G_f(K J/mol)$
20.4936	1.67E-04	2.20E-05	13.9918	6.36E+05	-32.9552
20.6279	1.74E-04	4.62E-05	13.8575	3.00E+05	-31.1010
20.7448	1.80E-04	6.91E-05	13.7406	1.99E+05	-30.0891
20.8834	1.87E-04	9.76E-05	13.6020	1.39E+05	-29.2128
21.0244	1.94E-04	1.28E-04	13.4610	1.05E+05	-28.5130
21.1472	2.00E-04	1.57E-04	13.3382	8.49E+04	-27.9896
20.4936	1.67E-04	2.20E-05	13.9918	6.36E+05	-32.9552
20.6279	1.74E-04	4.62E-05	13.8575	3.00E+05	-31.1010
20.7448	1.80E-04	6.91E-05	13.7406	1.99E+05	-30.0891
$\Lambda_M=34.48549 cm^2.Ohm^{-1}$ $\Lambda_{ML}=20.36157$					

**Table 6.** Formation constants and Gibbs free energies of formation for 1:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 293.15 K

$\Lambda_{obs}(cm^2.Ohm^{-1})$	[L]	$(\Lambda_{obs} - \Lambda_{ML})[L]$	$(\Lambda_M - \Lambda_{obs})$	$K_f$	$\Delta G_f(K J/mol)$
19.1448	9.09E-05	1.34E-05	15.3406	1.14E+06	-34.3999
19.2952	9.91E-05	2.96E-05	15.1902	5.14E+05	-32.4312
19.4289	1.07E-04	4.63E-05	15.0565	3.26E+05	-31.3049
19.5625	1.15E-04	6.50E-05	14.9229	2.29E+05	-30.4426
19.6985	1.23E-04	8.61E-05	14.7869	1.72E+05	-29.7264
19.8196	1.30E-04	1.07E-04	14.6658	1.37E+05	-29.1653
19.9605	1.38E-04	1.33E-04	14.5249	1.09E+05	-28.6138
20.0858	1.45E-04	1.58E-04	14.3996	9.10E+04	-28.1618
20.2317	1.53E-04	1.88E-04	14.2537	7.57E+04	-27.7075
20.3615	1.60E-04	2.18E-04	14.1239	6.48E+04	-27.3245
19.1448	9.09E-05	1.34E-05	15.3406	1.14E+06	-34.3999
19.2952	9.91E-05	2.96E-05	15.1902	5.14E+05	-32.4312
$\Lambda_M=34.48549 cm^2.Ohm^{-1}$ $\Lambda_{ML}=18.99706$					

**Table 7.** Formation constants and Gibbs free energies of formation for 2:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 293.15 K

$\Lambda_{obs}(cm^2.Ohm^{-1})$	[L]	$(\Lambda_{obs} - \Lambda_{ML})[L]$	$(\Lambda_M - \Lambda_{obs})$	$K_f$	$\Delta G_f(K J/mol)$
18.3796	4.76E-05	8.00E-06	16.1058	2.01E+06	-35.7973
18.5340	5.66E-05	1.83E-05	15.9514	8.74E+05	-33.7400
18.6737	6.54E-05	3.02E-05	15.8117	5.23E+05	-32.4742
18.8338	7.41E-05	4.61E-05	15.6516	3.39E+05	-31.4077
18.9970	8.26E-05	6.49E-05	15.4884	2.39E+05	-30.5396
$\Lambda_M=34.48549 cm^2.Ohm^{-1}$ $\Lambda_{ML}=18.21149$					

**Table 8.** Formation constants and Gibbs free energies of formation for 1:2 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 298.15 K

$\Lambda_{obs}(cm^2.Ohm^{-1})$	[L]	$(\Lambda_{obs} - \Lambda_{ML})[L]$	$(\Lambda_M - \Lambda_{obs})$	$K_f$	$\Delta G_f(K J/mol)$
28.4509	1.67E-04	3.30E-05	64.8976	1.97E+06	-35.7392
28.6524	1.74E-04	6.94E-05	64.6962	9.33E+05	-33.9013
28.8278	1.80E-04	1.04E-04	64.5208	6.22E+05	-32.9035
29.0357	1.87E-04	1.46E-04	64.3129	4.39E+05	-32.0443
29.2472	1.94E-04	1.92E-04	64.1014	3.33E+05	-31.3620
29.4314	2.00E-04	2.36E-04	63.9171	2.71E+05	-30.8542
28.4509	1.67E-04	3.30E-05	64.8976	1.97E+06	-35.7392
28.6524	1.74E-04	6.94E-05	64.6962	9.33E+05	-33.9013
28.8278	1.80E-04	1.04E-04	64.5208	6.22E+05	-32.9035
$\Lambda_M=93.34867 cm^2.Ohm^{-1}$ $\Lambda_{ML}=28.25291$					

**Table 9.** Formation constants and Gibbs free energies of formation for 1:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 298.15 K

$\Lambda_{obs}(cm^2.Ohm^{-1})$	[L]	$(\Lambda_{obs} - \Lambda_{ML})[L]$	$(\Lambda_M - \Lambda_{obs})$	$K_f$	$\Delta G_f(K J/mol)$
26.4127	9.09E-05	1.95E-05	66.9359	3.43E+06	-37.1102
26.6315	9.91E-05	4.30E-05	66.7171	1.55E+06	-35.1576
26.8502	1.07E-04	6.99E-05	66.4984	9.52E+05	-33.9507
27.0543	1.15E-04	9.85E-05	66.2943	6.73E+05	-33.0963
27.2584	1.23E-04	1.30E-04	66.0902	5.07E+05	-32.3998
27.4401	1.30E-04	1.62E-04	65.9085	4.07E+05	-31.8550
27.6513	1.38E-04	2.00E-04	65.6973	3.28E+05	-31.3219
27.8393	1.45E-04	2.39E-04	65.5093	2.75E+05	-30.8858
28.0581	1.53E-04	2.84E-04	65.2900	2.30E+05	-30.4498
28.2529	1.60E-04	3.28E-04	65.0957	1.98E+05	-30.0830
26.4127	9.09E-05	1.95E-05	66.9359	3.43E+06	-37.1102
26.6315	9.91E-05	4.30E-05	66.7171	1.55E+06	-35.1576
$\Lambda_M=93.34867 cm^2.Ohm^{-1}$ $\Lambda_{ML}=26.19788$					

**Table 10.** Formation constants and Gibbs free energies of formation for 2:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 298.15 K

$\Lambda_{\text{obs}}(\text{cm}^2\cdot\text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]$	$(\Lambda_{\text{M}} - \Lambda_{\text{obs}})$	$K_f$	$\Delta G_f(\text{K J/mol})$
25.3252	4.76E-05	1.05E-05	68.0234	6.48E+06	-38.6812
25.5248	5.66E-05	2.38E-05	67.8238	2.85E+06	-36.6574
25.7535	6.54E-05	4.24E-05	67.5951	1.59E+06	-35.2209
25.9867	7.41E-05	6.54E-05	67.3619	1.03E+06	-34.1472
26.1978	8.26E-05	9.03E-05	67.1507	7.44E+05	-33.3423
$\Lambda_{\text{M}}=93.34867 \text{ cm}^2\cdot\text{Ohm}^{-1}$ $\Lambda_{\text{ML}}=25.1047$					

**Table 11.** Formation constants and Gibbs free energies of formation for 1:2 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 303.15 K

$\Lambda_{\text{obs}}(\text{cm}^2\cdot\text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]$	$(\Lambda_{\text{M}} - \Lambda_{\text{obs}})$	$K_f$	$\Delta G_f(\text{K J/mol})$
49.7752	1.67E-04	3.68E-05	101.9327	2.77E+06	-36.5884
50.1557	1.74E-04	1.04E-04	101.5522	9.73E+05	-34.0062
50.4870	1.80E-04	1.68E-04	101.2209	6.02E+05	-32.8218
50.8797	1.87E-04	2.48E-04	100.8282	4.07E+05	-31.8553
51.2792	1.94E-04	3.34E-04	100.4287	3.01E+05	-31.1113
51.6272	2.00E-04	4.15E-04	100.0807	2.41E+05	-30.5679
49.7752	1.67E-04	3.68E-05	101.9327	2.77E+06	-36.5884
50.1557	1.74E-04	1.04E-04	101.5522	9.73E+05	-34.0062
50.4870	1.80E-04	1.68E-04	101.2209	6.02E+05	-32.8218
$\Lambda_{\text{M}}=151.708 \text{ cm}^2\cdot\text{Ohm}^{-1}$ $\Lambda_{\text{ML}}=49.55476$					

**Table 12.** Formation constants and Gibbs free energies of formation for 1:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 303.15 K

$\Lambda_{\text{obs}}(\text{cm}^2\cdot\text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]$	$(\Lambda_{\text{M}} - \Lambda_{\text{obs}})$	$K_f$	$\Delta G_f(\text{K J/mol})$
45.8162	9.09E-05	1.67E-05	105.8917	6.32E+06	-38.6207
46.2030	9.91E-05	5.66E-05	105.5049	1.86E+06	-35.6089
46.5968	1.07E-04	1.03E-04	105.1112	1.02E+06	-34.1149
46.9976	1.15E-04	1.57E-04	104.7103	6.67E+05	-33.0730
47.4058	1.23E-04	2.18E-04	104.3021	4.79E+05	-32.2566
47.7691	1.30E-04	2.79E-04	103.9388	3.73E+05	-31.6403
48.1915	1.38E-04	3.53E-04	103.5164	2.93E+05	-31.0475
48.5676	1.45E-04	4.27E-04	103.1403	2.42E+05	-30.5715
49.0051	1.53E-04	5.14E-04	102.7028	2.00E+05	-30.0992
49.3947	1.60E-04	6.01E-04	102.3132	1.70E+05	-29.7064
45.8162	9.09E-05	1.67E-05	105.8917	6.32E+06	-38.6207
46.2030	9.91E-05	5.66E-05	105.5049	1.86E+06	-35.6089
$\Lambda_{\text{M}}=151.708 \text{ cm}^2\cdot\text{Ohm}^{-1}$ $\Lambda_{\text{ML}}=45.632$					

**Table 13.** Formation constants and Gibbs free energies of formation for 2:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 303.15 K

$\Lambda_{\text{obs}}(\text{cm}^2\cdot\text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]$	$(\Lambda_{\text{M}} - \Lambda_{\text{obs}})$	$K_f$	$\Delta G_f(\text{K J/mol})$
43.8485	4.76E-05	5.31E-06	107.8594	2.03E+07	-41.4996
44.2455	5.66E-05	2.88E-05	107.4624	3.73E+06	-37.3217
44.6048	6.54E-05	5.68E-05	107.1031	1.89E+06	-35.6389
45.0164	7.41E-05	9.48E-05	106.6915	1.13E+06	-34.3639
45.4362	8.26E-05	1.40E-04	106.2718	7.57E+05	-33.3867
$\Lambda_{\text{M}}=151.708 \text{ cm}^2\cdot\text{Ohm}^{-1}$ $\Lambda_{\text{ML}}=43.737$					

**Table 14.** Formation constants and Gibbs free energies of formation for 1:2 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 308.15 K

$\Lambda_{\text{obs}}(\text{cm}^2\cdot\text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]$	$(\Lambda_{\text{M}} - \Lambda_{\text{obs}})$	$K_f$	$\Delta G_f(\text{K J/mol})$
63.3853	1.67E-04	2.14E-05	100.8496	4.72E+06	-37.8992
63.8335	1.74E-04	1.00E-04	100.4014	1.00E+06	-34.0809
64.2818	1.80E-04	1.85E-04	99.9531	5.41E+05	-32.5577
64.8131	1.87E-04	2.91E-04	99.4218	3.42E+05	-31.4243
65.3536	1.94E-04	4.06E-04	98.8813	2.44E+05	-30.5913
65.8245	2.00E-04	5.13E-04	98.4104	1.92E+05	-29.9983
63.3853	1.67E-04	2.14E-05	100.8496	4.72E+06	-37.8992
63.8335	1.74E-04	1.00E-04	100.4014	1.00E+06	-34.0809
64.2818	1.80E-04	1.85E-04	99.9531	5.41E+05	-32.5577
$\Lambda_{\text{M}}=164.235 \text{ cm}^2\cdot\text{Ohm}^{-1}$ $\Lambda_{\text{ML}}=63.257$					

**Table 15.** Formation constants and Gibbs free energies of formation for 1:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 308.15 K

$\Lambda_{\text{obs}}(\text{cm}^2.\text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}} - \nu_{\text{ML}})[L]$	$(\Lambda_{\text{M}} - \Lambda_{\text{obs}})$	$K_f$	$\Delta G_f(\text{K J/mol})$
58.0858	9.09E-05	9.70E-06	106.1491	1.09E+07	-39.9729
58.6015	9.91E-05	6.17E-05	105.6334	1.71E+06	-35.3993
59.1265	1.07E-04	1.23E-04	105.1084	8.55E+05	-33.6872
59.6610	1.15E-04	1.93E-04	104.5739	5.41E+05	-32.5560
60.2052	1.23E-04	2.73E-04	104.0297	3.81E+05	-31.6899
60.6896	1.30E-04	3.53E-04	103.5453	2.93E+05	-31.0447
61.2529	1.38E-04	4.51E-04	102.9821	2.28E+05	-30.4277
61.7543	1.45E-04	5.49E-04	102.4806	1.87E+05	-29.9350
62.3376	1.53E-04	6.65E-04	101.8973	1.53E+05	-29.4476
62.8571	1.60E-04	7.79E-04	101.3778	1.30E+05	-29.0435
58.0858	9.09E-05	9.70E-06	106.1491	1.09E+07	-39.9729
58.6015	9.91E-05	6.17E-05	105.6334	1.71E+06	-35.3993
$\Lambda_{\text{M}}=164.235 \text{ cm}^2.\text{Ohm}^{-1}$ $\nu_{\text{ML}}=57.979$					

**Table 16.** Formation constants and Gibbs free energies of formation for 2:1 (M/L) CoCl<sub>2</sub>-L1 complexes in ethanol at 308.15 K

$\Lambda_{\text{obs}}(\text{cm}^2.\text{Ohm}^{-1})$	[L]	$(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[L]$	$(\Lambda_{\text{M}} - \Lambda_{\text{obs}})$	$K_f$	$\Delta G_f(\text{K J/mol})$
55.4621	4.76E-05	4.29E-06	108.7728	2.53E+07	-42.0447
55.9915	5.66E-05	3.51E-05	108.2434	3.09E+06	-36.8527
56.4705	6.54E-05	7.18E-05	107.7644	1.50E+06	-35.0726
57.0194	7.41E-05	1.22E-04	107.2155	8.78E+05	-33.7526
57.5790	8.26E-05	1.82E-04	106.6559	5.85E+05	-32.7507
$\Lambda_{\text{M}}=164.235 \text{ cm}^2.\text{Ohm}^{-1}$ $\Lambda_{\text{ML}}=55.372$					

**Table 17.** The Entropy changes (TAS) of CoCl<sub>2</sub> in absolute ethanol at 293.15, 298.15, 303.15 and 308.15 K were calculated by applying the equation;  $\Delta G = \Delta H - T\Delta S$ 

		$\Delta G_A$				$(TAS)_A$			
	$\Delta H_A$	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
(2:1)	21.7094	-6.488	-7.015	-7.655	-8.093	28.19741	28.7244	29.3644	29.8024
(1:1)	24.8133	-6.133	-6.647	-7.269	-7.684	30.94636	31.4603	32.0823	32.4973
(1:2)	25.5275	-5.474	-5.924	-6.462	-6.835	31.00154	31.4515	31.9895	32.3625
		$\Delta G_f$				$(TAS)_f$			
	$\Delta H_f$	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
(2:1)	22.9524	-35.797	-38.681	-41.499	-42.044	131.6064	134.4903	137.3087	137.8537
(1:1)	25.9500	-34.399	-37.111	-38.621	-39.973	145.7051	148.4155	149.9260	151.2782
(1:2)	27.4458	-32.955	-35.739	-36.588	-37.899	150.4672	153.2512	154.1004	155.4112

The obtained values ( $K_f$ ) for CoCl<sub>2</sub>-ligand stoichiometric complexes are presented in tables 2,3. The Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation:

$$\Delta G_f = -RT \ln K_f$$

The calculated  $\Delta G_f$  values are presented in tables (5-16).

The enthalpy change( $\Delta H$ ) and the entropy change( $T\Delta S$ ) evaluated for CoCl<sub>2</sub>-ligand complexes indicate that (L1) may act as flexidentate ligand.

The Enthalpy change of association ( $\Delta H_A$ ), and the Enthalpy change of formation ( $\Delta H_f$ ) of CoCl<sub>2</sub> in absolute ethanol at 293.15, 298.15, 303.15 and 308.15 K estimated by plotting  $\log K_A$  and  $\log K_f$  for different M/L concentrations for (2:1), (1:1) and (1:2) stoichiometric complexes against  $1/T$  are represented in (figs. 7,8).

## 4. Conclusions

This work concentrated on the behaviour of CoCl<sub>2</sub> with the ligand conductometrically. The main target is to discuss the complexation between the metal and ligand for evaluating different concentrations from the metal ion in different solutions.

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