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### Electrical conductivity of some cobalt (III) complex salts in aqueous medium at 298 K

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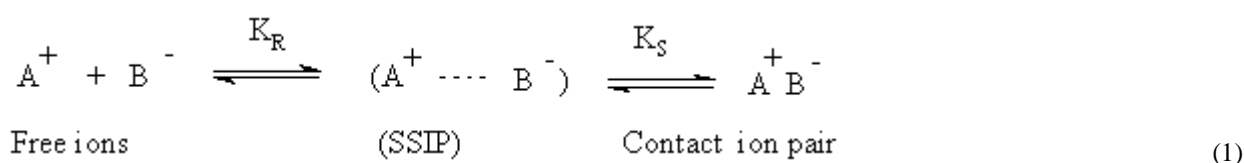
#### ABSTRACT

The conductance of two different symmetrical complexes cobalt(III) tetramine oxalato  $[Co_{(3,2,3)}tetOx]X$  and trien carbonato  $[Co(tn)_2CO_3]X$  ( where  $X=Cl, Br, I, ClO_4^-$  and  $PF_6^-$  ), in water are determined at 298 K. The results are analyzed by Fuoss-Onsager model to estimate simultaneously molar infinity of conductance  $\Lambda_o$ , association constant  $K_A$  and associated parameter distances of ion pairs  $R$ , (all related to standard minimum deviation  $\sigma_A$ ). Data are applied to calculate the solvated ionic radii and solvation number, according to Gill' equation which revealed that solvent separated ion pair (SSIP) model is preferred to these complexes aqueous medium.

**Keywords:** Electrical conductivity, Co(III)complexes association, Gill's radii, transport number, solvation numbers.

#### INTRODUCTION

Gurney (1) explained ion pair model by including both contact and solvent-separated (SSIP) ion pairs as represented in the following equation:



where  $K_S$  describes the formation and separation of contact pairs by a series of inter changes of sites between solvent molecules and ions. This term depends on short-range ion-solvent interaction and is different for structurally different solvents;  $K_R$  describes the formation and separation of solvent-separated pairs by diffusion in and out of co-spheres of diameter  $R$  around ions. Prue (2) stated that the general boundary conditions were independent of short-range effects where ions were surrounded by spheres with diameter  $R$  outside of which the solvent was described electrostatically by its microscopic dielectric constant and hydrodynamically by its bulk viscosity. Ions were counted as nonconducting ion pairs and deleted from the population of atmospheric ions.

Fuoss (3) suggested a model which separated the problems of correlating  $\Lambda_o$  and  $K_A$  with molecular parameters from the treatment of long range electrostatic and hydrodynamic interactions. According to Fuoss hypothesis, the three adjustable parameters  $\Lambda_o$ ,  $K_A$  and  $R$  were obtained by applying the following equations:

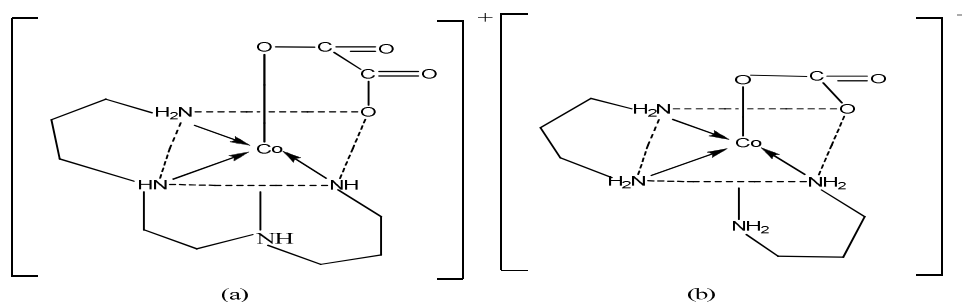
$$\Lambda = (\Lambda_o - \Delta\Lambda_e) (1 + \Delta X/X) \quad (2)$$

$$K_A (1 - \gamma) / C \gamma^2 f_{\pm}^2 = K_R (1 + K_S) \quad (3)$$

$$\text{and } -\ln f_{\pm} = \beta K / 2(1 + K R) \quad (4)$$

where  $K_R = 4\pi NR^3/3000 \exp \beta/R$ ,  $\beta = e^2/\epsilon kT$  and  $R = co$  sphere diameter describing the different controlled steps in the equilibria of equation (1) where  $\epsilon =$ the dielectric constant for given medium. Using the hard sphere in a continuum model,  $\Delta\Lambda_e$  are identified by the electrophoretic effect and the relaxation effect  $\Delta X/X$ . The fraction  $(1-\gamma)$  of solute existed as ion pairs in the above equilibriums.

One of the major interests in coordination chemistry is to study the interaction between central atom and surrounding atoms, ions or molecules. Coordination compounds containing ligands have been known a long time ago. Exceptional stability of complexes can be attributed to their charge distribution which is stabilized by hydrogen bonding. Two different ligating nitrogen atoms of amino ligands in the equatorial of the coordination octahedron like (a) N'[2-(3-amino propylaminoethyl)]propane-1,3- diamine= (3,2,3 tet) to form Co(III)oxalato tetramines complexes and (b) propane -1,2 -clamine= (tn) to form Co(III) carbonato complexes. Structural formula of the above two amino complex ions are illustrated in Scheme 1



Scheme 1: Structure of (a) [Co(III)(3,2,3tet)Ox] and (b) [Co(tn)<sub>2</sub>CO<sub>3</sub>] complexes

Many Authors(4-7) studied the conductance of symmetrical complexes at different solvents and at different temperatures. In the present investigation, the electrical conductivity parameters  $\Lambda_0$ ,  $K_A$  and  $R$  of the above two cationic complexes with common series of anions like  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$  and  $PF_6^-$  in aqueous solutions at 298 K were chosen to study the effect of varying cationic and anionic groups on the conductance behaviour.

## MATERIALS AND METHODS

The octahedral structure of carbonato- and oxalato tetramine cobalt Co(III) chloride, bromide, iodide, perchlorate and phosphorus hexafluoride complexes were prepared and characterized as described by Massoud et al( 8). The crude products were recrystallized twice from double distilled H<sub>2</sub>O and dried in vacuum at 80 °C till constant weight then kept in vacuum desiccators.

Conductivity water was obtained by passing freshly distilled H<sub>2</sub>O through 60 cm long Elgastat deionizer, while guarding against atmospheric CO<sub>2</sub> by using a soda lime tube. Measurement of specific conductance  $K_o$  amounted to  $5.7 \times 10^{-7} S cm^{-1}$ , density ( $d$ ) was  $0.99704 g dm^{-3}$  while viscosity  $\zeta$  was  $0.8937 cP$  for pure H<sub>2</sub>O as reported ( 9,10).

An Erlenmeyer conductivity cell with bright Pt electrodes having a cell constant of  $0.04056 \pm 0.33\% cm^{-1}$  was used. Conductance measurements were performed using an a.c. Beckman conductivity bridge(RC 18A) with accuracy of  $\pm 0.1$  for resistance and ac frequency of 3 k Hz where temperature was adjusted to  $298 \pm 0.02 K$  with a Haake NB 22 Ultrathermostate. The runs were carried out as reported (11,12).

## RESULTS AND DISCUSSION

Preliminary limiting molar conductance  $\Lambda_0$  of the cobalt oxalato [Co(3,2,3tet)OX]X and cobalt carbonato [Co(tn)<sub>2</sub>CO<sub>3</sub>]X complexes[X= Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>] in aqueous solutions at 298 K were obtained by extrapolating the molar conductance  $\Lambda$  versus  $\sqrt{C}$  at zero concentration. Tables 1 and 2 record the data related to concentration (C) against equivalent conductance( $\Lambda$ ) of oxalato and carbonato systems, respectively.. The preliminary  $\Lambda_0$  values were taken as an input in Fuoss-Onsager(13) conductance equation to obtain simultaneously the three adjustable parameters  $\Lambda_0$ ,  $K_A$  and  $R$ . Data were analyzed using a Scan computer program provided by Fuoss that minimized the standard deviation  $\sigma_\Lambda$ ; equation 5:

$$\sigma_\Lambda = \sqrt{\frac{\sum[\Lambda_{calc} - \Lambda_{exp}]^2}{(n-2)}} \quad (5)$$

Table (3) demonstrates that  $\Lambda_0$  of oxalato salt solutions were increased in the order  $\text{Br}^- > \text{Cl}^- > \text{I}^- > \text{ClO}_4^- > \text{PF}_6^-$  while for carbonato salts, the order for  $\Lambda_0$  was  $\text{I}^- > \text{Cl}^- > \text{ClO}_4^- > \text{PF}_6^-$ .

Several studies were carried out on conductance behaviour of Co(III) complexes at different solutions (14). Ramadan et al(12) estimated  $\Lambda_0$  of  $[\text{Co}(\text{en})_2\text{CO}_3]\text{ClO}_4$  in water at 298 K and found to be  $93.82 \text{ Scm}^2 \text{ mol}^{-1}$  while in this study,  $\Lambda_0$  value of  $\text{Co}(\text{tn})_2\text{CO}_3]\text{ClO}_4$  under the same conditions was found to be  $92.7 \text{ S cm}^2 \text{ mol}^{-1}$  Table 3, indicating that small difference by one  $\text{CH}_2$  group in amino ligand structure led to a large variation in conductance. This change was attributed to high solvation by hydrogen bonding between the extra  $\text{NH}_2$  group and water molecule, with solvophobic structure-making processes by water around the hydrocarbon parts of ligands for both the oxalato and carbonato complexes resulting from hydrophobicity of coordinated ligands (15).

$$\text{Since } \Lambda_0 = v_+ \lambda_o^+ + v_- \lambda_o^- \quad (6)$$

where  $v_+$  and  $v_-$  = the number of cations and anions per molecule ( $v_+ = v_- = 1$ , for univalence electrolytes),  $\lambda_o^+$  and  $\lambda_o^-$  = the limiting conductance for cation and anion respectively at infinite dilution. In this study  $\lambda_o^-$  values for anions were taken from literature [6,14] as subtracted from the related  $\Lambda_0$  to give cationic  $\lambda_o^+$  value. The approximate limiting cations  $\lambda_o^+$  values for Co(III) oxalato and carbonato complexes were found to be 24.14 and 24.24  $\text{Scm}^2 \text{ mol}^{-1}$  respectively Table 4. This indicated that both cations had similar solvation process.

### Ionic Association

A glance view to  $K_A$  values in Table 3, revealed that  $K_A$  had moderately low values in Scheme 2. both series of the studied complexes and ranged between (10.47 and 12.94) indicating weak ion pairing that slightly varied with varying anionic species in the order  $\text{PF}_6^- < \text{ClO}_4^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$  for oxalato complex and  $\text{ClO}_4^- < \text{Cl}^- < \text{PF}_6^- < \text{I}^-$  for carbonato complex.  $K_A$  showed a change due to relative binding strength of anion to the octahedron cationic skeleton

Additional effect might have been involved which was specific for a given ion-solvent system. The moderate  $K_A$  values, observed for the above complexes revealed that the short-range interaction between the cation and anion was also moderately due to large size and low charge densities that surrounded the cations, besides highly stable solvated anions.

Tasic et al (15) found that  $K_A$  for Rb cyclohexylsulfamate was 0.9 while that for Cs cyclohexylsulfamate was 6.8  $\text{dm}^3 \text{ mol}^{-1}$  in water indicating high sensitive association of solvated alkali metals relative to greatest stability of anion size (cyclohexylsulfamate).

Kawana (16) measured the conductance of s-acetylthiocholine halides and perchlorate in aqueous solutions at different temperatures and found that  $K_A$  was higher in  $\text{ClO}_4^-$  than in  $\text{Br}^-$  complexes. Dash et al(17) reported larger  $K_A$  value for  $\text{Br}^-$  in trans  $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$ , which attributed to less ionic stability and lack of solvation of ions although trans  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  gave smaller ion pair association.

Gibbs free energy of association could be given by the following equation

$$\Delta G = -RT \ln K_A(m) \quad (7)$$

where  $K_A(m)$  is in molality scale. Since  $G_s = \Delta G/RT$  so, then

$$G_s = -\ln K_A \quad (8)$$

Table 3 shows that all Gibbs free energy values were negative, Fuoss discussed  $G_s$  in term of  $\Delta H$  and  $-\Delta S$  since the enthalpy contained the work done in separating a contact pair to infinity given negative part of enthalpy. The enthalpy also contained a positive term due to replacement of nearest neighbouring solvent molecules by partner ion in the last step in the function of contact pair. Since two unpaired ions can be represented by many configurations whereas a contact ion pair had less degree of freedom, so the entropy term decreased, and  $-\Delta S$  was positive. According to the previous picture the approximate negativity of  $G_s$  term for all complexes were related to the electrostatic part of enthalpy.

Generally, the increase in negativity of  $G_s$  term (Table 3) for the studied two series of complexes revealed an increase in the electrostatic part of enthalpy in the direction of related complexes as  $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{ClO}_4^- < \text{PF}_6^-$ . It may be concluded that the differences in  $G_s$  were due to different influences on water structure around each

complex cation. De -visser and Somsen (18 ) attributed the preference of tetraalkyl ammonium bromide for water to hydrophobic bonding of the cation.

### **Ionic radii**

Several studies (14,19) reported on the relation between solvated ionic radius ( $r_i$ ) and the properties of the solvent, mainly viscosity  $\eta$  and dielectric constant  $\epsilon$

Gill (20 ) modified the Stokes' law from which the ionic solvated radius ( $r_s$ ) of diffusing ions had been calculated using the following equation

$$r_s = (Z) F^2 / 6 \pi N \lambda_0 \eta = 0.819 (Z) / \lambda_0 \eta = 0.732 \cdot 10^{-8} T / D \eta \quad (9)$$

where (Z) = absolute charge of the ion, and D = limiting ionic diffusion coefficient .

The new modified form depended on inserting a correction factor containing the dielectric constant. In this treatment ,Gill considered the assumption of Stokes as well as Nightingale(21)for looking to  $\text{Me}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ ,  $\text{Bu}_4\text{N}^+$  and  $\text{Am}_4\text{N}^+$  as unsolvated cations in water was not correct.  $\text{Me}_4\text{N}^+$  was found to be a structure breaker in water(22) and exhibited solvation in many non-aqueous solvents(23)due to its valuable charge density. On the other hand ,  $\text{Pr}_4\text{N}^+$ ,  $\text{Bu}_4\text{N}^+$  and  $\text{Am}_4\text{N}^+$  ions were found to act as excellent structure makers(22,24). In this case, the charge to surface ratio was too small to allow for permanent orientation of water (the dipoles) in the first hydration sheath. Solvation was attributed to hydrophobic hydration around the hydrocarbon chains of these ions (25) .Gill looked at  $\text{Et}_4\text{N}^+$  as an intermediate between  $\text{Me}_4\text{N}^+$  and  $\text{Pr}_4\text{N}^+$   $\text{Bu}_4\text{N}^+$  and  $\text{Am}_4\text{N}^+$  ,hence it could be considered as unsolvated ion and its radius in solution was taken as the crystallographic one.

According to the previous picture, Gill(20) suggested the following equation

$$r_i = r_s + r_x \quad (10)$$

where  $r_i$  = ionic radius in solution ,  $r_s$  = Stokes radius and  $r_x$  = correction factor which when plotted against the dielectric constant  $\epsilon$  , for several non-aqueous solvents ,two parallel lines were obtained and satisfy the relation

$$r_x = 0.0103 \epsilon + r_y \quad (11)$$

where  $r_y = 1.13 \text{ \AA}$  for the hydrogen bonded solvents and highly associated dipolar aprotic solvents. The applicability of Gill's equation to calculate  $r_i$  or  $\lambda_+$  and  $\lambda_-$  was proved by several systems[26,27].In this study ,the anionic radius for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ , and  $\text{PF}_6^-$  in addition to the cations  $[\text{Co}_{(3,2,3)} \text{ tet Ox}]^+$  and  $[\text{Cotn}_2 \text{ CO}_3]^+$  , could be calculated in water using equation(12) in the collected form

$$r_i = (0.819(Z)/\eta\lambda) + 0.0103\epsilon + r_y \quad (12)$$

Summation of the hydrodynamic radii ( $r_i^+ + r_i^-$ ) would be compared with the distance (R) obtained previously from Fuoss as showed in equation (3).

Table 4 records the estimated  $r^+$  and  $r^-$  values from equation (12) for oxalato and carbonato Co(III) complexes in addition to the related experimental values (R) . The behavior of R as the summation in sizes of the radii corrected by Gill ( $r^+ + r^-$ ) confirmed the hypothesis that the anion –solvent dipole interaction was predominantly in electrolytes with common cation. It could be readily seen that the experimental R values were greater than summation of the obtainable electrostatic Gill radii ( $r^+ + r^-$ ). This would mean that Gurney co-sphere model could be considered for the above complexes where  $K_A$  in this model represented more than one non-conducting ion pairs bonded by short-range interactions and coincided in one sphere as represented in Fig. 1.

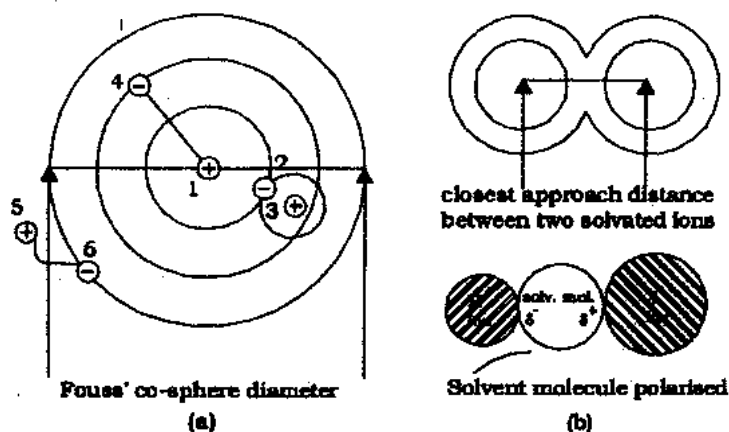


Fig. 1 . (a) Probabilities of R values (b) Formation of (SSIP)

The individual ions should be separated by at least one water molecule to give solvent-separated ion-pair model (SSIP) as previously reported by Evans and Gardam(26). Lee and Wheaton(27) extended the above model suggesting that when a cation  $M^+$  and anion  $X^-$  were separated by a single solvent molecule, the stability of  $M^+(\text{solv.})X^-$  ion pair will depend on the polarizing power of  $M^+$  and  $X^-$  ions as well as the polarizability of the solvent molecules that has been controlled by equation(3).

Bernal et al(28) reported that  $[\text{Co}(\text{tn})_2\text{CO}_3]^+$  and  $\text{ClO}_4^-$  had radii of 9.9 and 2.4 Å respectively, where their summation equated 12.3 Å. In our case, experimental R values, ranged between (13.8- 15.2) Å at 298 K as recorded in Table 4, indicating that ion-pairing process would put these complexes in the class of solvated ion-pairs by one or two water molecules where ( $\delta_{\text{OH}^-}$ ) had the diameter of  $\text{OH}^-$  equalled to 2.8 Å (29). The limitation of ion pair solvation in water was given by Barthel et al[ 30] expression as

$$r = r_i^+ + r_i^- + \delta_{\text{OH}^-} \quad (13)$$

The data in Table 4 show that  $r_i$  for anion solvation had followed the trend of  $\text{Cl}^- < \text{Br}^- = \Gamma^- < \text{PF}_6^- < \text{ClO}_4^-$  for both complexes while  $r_i$  for solvated two cations had nearly the same values as expected. This behaviour could be explained on the basis that hydrogen bonding interaction of water to cation in weakly charged complexes was an extreme case of an ion-dipole electrostatic interaction.

It must be mentioned here that (R) which was the cosphere diameter containing both contact and non-contact pairs, represented both short and long ranges interactions, Fig. 1.

### Transport number

The experimental results showed that transport numbers were generally concentration dependent. In the case of non-associated 1:1 electrolytes, the form of concentration dependence was as follows ;(a) if the transport number of ion was close to 0.5, it scarcely varied with concentration, (b) if the ion transport number was less than 0.5, it increased further with increasing concentration and (c) if the ion transport number was greater than 0.5, it decreased with concentration( 6 ). These findings were completely and quantitatively explained by the interionic attraction theory (31). The following equation would fit the purpose for calculating the transport number( $t_i$ ) of the given ions i from which  $t_i^0$ (the limiting transport number) could be calculated by extrapolating  $t_i$  vs  $\sqrt{c}$  line into zero concentration

$$t_i = \frac{\lambda_0 - \frac{1}{2}[zi]B_2\sqrt{I}/(1+ka)}{\lambda_0 - [zi+zj]B_2\sqrt{I}/(1+ka)} \quad (14)$$

where  $B_2 = 82.5/\eta (\epsilon T)^{1/2}$ ,  $k = Ba\sqrt{I}$ ,  $B = 50.29 \times 10^8 / (\epsilon T)^{1/2}$  and  $a =$  closest approach distance of the two ions i and j.

For 1:1 electrolytes, the above equation, could be simplified to :

$$t_i = \frac{\lambda_0 - \frac{1}{2}B_2\sqrt{c}/(1+ka)}{\lambda_0 - B_2\sqrt{c}/(1+ka)} \quad (15)$$

Equation (15) gave an excellent quantitative account of the observed transport number.

Based on the above equation data in , Table 5 showed  $t_x^o$  values for the anions of our complexes in water at 298 K .It could be seen that  $t_x^o$  for the anions with respect to oxalato complex followed the order,  $Br^- > I^- > Cl^- > ClO_4^- > PF_6^-$  ,while that for carbonato complex obeyed the order  $Cl^- > I^- > PF_6^- > ClO_4^-$ . In both series ,the degree of hydrogen bonding had a significant influence on the ionic mobility.

When taking average  $t_x^o$  related to halides only or between  $ClO_4^-$  and  $PF_6^-$  values in both series, the limiting transport number for the related cation could be estimated and found that it obeyed  $t_{Co-CO_3}^o > t_{Co-oxalt}^o$ , Table 5 .

**Solvation number**

The volume of net solvation shell was instructed by Paul et al (32 ) that given as

$$V_s = 4/3 \pi (r_i^3 - r_x^3) \tag{16}$$

Where  $r_i$  and  $r_x$  were the solvated and crystallographic radii respectively ,  $r_x$  was taken from literatures (16, 20, 22), found to be 1.81, 1.95, 2.16 and 2.88 Å for  $Cl^-$ ,  $Br^-$ ,  $I^-$ , and  $ClO_4^-$  respectively as showed in Table(4).

Accordingly the solvation number( $n_s$ ) for each ion could be obtained from equation (17)

$$n_s = V_s / V_m \tag{17}$$

where  $V_m$  was the partial molar volume of the given solvent, in more common solvent used as water, its value was known as (18 mol dm<sup>-3</sup>). Table 4 collected in the estimated salvation numbers of the above ions. In this field ions could be classified (33) either with high charge density known as structure maker ions ; with small charge density known as structure breakers ions and those with extremely small charge density containing alkyl or aryl groups known as hydrophobic structure-makers. In this field  $Cl^-$ ,  $Br^-$  and  $I^-$  belonged to the first type while  $ClO_4^-$  was related to second type .The calculated solvation numbers were found to be varied in the same trend with varying their limiting conductance values.

TABLE I: Conductance of [Co(3,2,3)tet.Ox]X complex salts at different concentrations in water at 298 K

[Co(3,2,3 tet)Ox]Cl		[Co(3,2,3 tet)OX]Br		[Co(3,2,3 tet)Ox]I	
10 <sup>4</sup> C/mol dm <sup>-3</sup>	Λ / S cm <sup>2</sup> mol <sup>-1</sup>	10 <sup>4</sup> C/ mol dm <sup>-3</sup>	Λ / S cm <sup>2</sup> mol <sup>-1</sup>	10 <sup>4</sup> C/ mol dm <sup>-3</sup>	Λ / S cm <sup>2</sup> mol <sup>-1</sup>
48.303	95.722	47.61	97.534	45.024	97.621
36.00	96.431	30.25	98.411	25.10	98.351
25.0	97.215	19.003	98.910	18.49	98.608
12.25	98.311	12.25	99.700	16.00	98.705
7.563	98.836	9.302	99.851	10.563	99.151
4.001	99.422	7.290	100.12	6.25	99.332
1.103	100.01	5.290	100.42	4.00	99.524
[Co(3,2,3 tet)Ox]ClO <sub>4</sub>			[Co(3,2,3 tet)Ox]PF <sub>6</sub>		
10 <sup>4</sup> C/ mol dm <sup>-3</sup>	Λ/S cm <sup>2</sup> mol <sup>-1</sup>	10 <sup>4</sup> C/ mol dm <sup>-3</sup>	Λ/S cm <sup>2</sup> mol <sup>-1</sup>	10 <sup>4</sup> C/ mol dm <sup>-3</sup>	Λ/S cm <sup>2</sup> mol <sup>-1</sup>
39.438	88.932	41.6025	89.211		
21.623	89.822	23.1361	89.698		
17.598	89.913	18.9225	89.765		
12.25	90.426	16.1684	90.098		
7.2361	90.707	11.0889	90.379		
5.29	90.931	6.5025	90.455		
2.9241	91.112	4.9723	90.697		

TABLE II: Conductance of [Co(tn)<sub>2</sub>.CO<sub>3</sub>]X complex salts at different concentrations in water at 298 K.

X= Cl <sup>-</sup>		X=I <sup>-</sup>		X= ClO <sub>4</sub> <sup>-</sup>		X=PF <sub>6</sub> <sup>-</sup>	
10 <sup>4</sup> C*	Λ <sup>§</sup>	10 <sup>4</sup> C	Λ	10 <sup>4</sup> C	Λ	10 <sup>4</sup> C	Λ
38.776	96.223	38.119	97.001	31.427	89.412	32.959	87.332
26.153	97.002	28.462	97.488	22.591	89.887	24.354	87.752
18.801	97.489	23.261	97.879	17.338	90.382	19.554	88.003
14.070	98.002	15.689	98.388	13.133	90.587	15.319	88.211
10.459	98.286	11.847	98.693	8.6200	91.004	10.272	88.697
5.480	99.014	6.8277	99.186	6.5076	91.179	5.5366	89.214
2.608	99.477	3.3269	99.612	2.8026	91.668	3.077	89.586

\* C= mol dm<sup>-3</sup> § Λ= S cm<sup>2</sup> mol<sup>-1</sup>

TABLE III: Conductance Parameters for Co(III)Oxalato and Carbonato Complex in Aqueous Solutions at 298 K [Co(3,2,3 tet) Ox]X

Complex	$\Lambda_0/S \text{ cm}^2 \text{ mol}^{-1}$	$K_A / \text{dm}^3 \text{ mol}^{-1}$	R/ $A^\circ$	-G <sub>s</sub> /k.J.mol <sup>-1</sup>	$10^{-2} \sigma_A$
[Co <sub>3,2,3 tetOx</sub> ]Cl	100.85	11.65	13.8	2.455	3.5
[Co <sub>3,2,3tet Ox.</sub> ] Br	101.71	12.55	13.9	2.5297	4.03
[Co <sub>3,2,3 tetOx.</sub> ] I	100.28	12.94	14.3	2.5603	4.94
[Co <sub>3,2,3 tetOx</sub> ] ClO <sub>4</sub>	92.00	10.47	14.9	2.3485	5.71
[Co <sub>3,2,3 tetOx</sub> ] PF <sub>6</sub>	91.65	11.22	15.1	2.4177	3.82

[Co (tn)<sub>2</sub> CO<sub>3</sub>]X

Complex	$\Lambda_0/S \text{ cm}^2 \text{ mol}^{-1}$	$K_A / \text{dm}^3 \text{ mol}^{-1}$	R / $A^\circ$	-G <sub>s</sub> / k .J.mol <sup>-1</sup>	$10^{-2} \sigma_A$
[Cotn <sub>2</sub> CO <sub>3</sub> ]Cl	100.312	11.07	13.9	2.4042	1.58
[Cotn <sub>2</sub> CO <sub>3</sub> ]I	100.55	12.93	14.0	2.5595	3.30
[Cotn <sub>2</sub> CO <sub>3</sub> ] ClO <sub>4</sub>	92.77	10.88	14.8	2.3869	2.82
[Cotn <sub>2</sub> CO <sub>3</sub> ] PF <sub>6</sub>	90.5	12.12	14.9	2.4949	2.31

TABLE IV: Parameters derived from conductance in aqueous solutions at 298 K .

## [Co(3,2,3 tet )Ox]X

Ion	$\lambda^0/S \text{ cm}^2 \text{ mol}^{-1}$	$r_s / A^\circ$	$r_f / A^\circ$	$(r_{f+} + r_{f-}) / A^\circ$	R/A <sup>o</sup>	n <sub>s</sub>
[Co(3,2,3 tet)Ox] <sup>+</sup>	24.14	3.798	5.735			-
Cl <sup>-</sup>	76.42 <sup>(a)</sup>	1.199	3.139	8.872	13.8	6.
Br <sup>-</sup>	77.7 <sup>(a)</sup>	1.18	3.124	8.855	13.9	5.
I <sup>-</sup>	76.28 <sup>(a)</sup>	1.202	3.142	8.877	14.8	5.
ClO <sub>4</sub> <sup>-</sup>	68.00 <sup>(b)</sup>	1.348	3.288	9.023	14.8	3.
PF <sub>6</sub> <sup>-</sup>	67.6 <sup>(b)</sup>	1.376	3.316	9.051	15.2	-

[Co(tn)<sub>2</sub> CO<sub>3</sub>]X

Ion	$\lambda^0/S \text{ cm}^2 \text{ mol}^{-1}$	$r_s / A^\circ$	$r_f / A^\circ$	$(r_{f+} + r_{f-}) / A^\circ$	R/A <sup>o</sup>	n <sub>s</sub>
[Cotn <sub>2</sub> CO <sub>3</sub> ] <sup>+</sup>	24.24	3.782	5.719	-	-	
Cl <sup>-</sup>	76.47	1.199	3.139	8.858	13.9	6
I <sup>-</sup>	76.28	1.202	3.142	8.861	14.0	5
ClO <sub>4</sub> <sup>-</sup>	68.00	1.348	3.288	9.007	14.8	3
PF <sub>6</sub> <sup>-</sup>	67.60	1.376	3.316	9.035	15.0	-

Ref(a) =6, Ref(b)=12

TABLE V: Limiting transference number t<sub>x</sub><sup>o</sup> of different ions in water at 298 K.

Ion	t <sub>x</sub> <sup>o</sup>	Ion	t <sub>x</sub> <sup>o</sup>
[Co(3,2,3tet)Ox] <sup>+</sup>	Av=0.239	[Co(tn) <sub>2</sub> CO <sub>3</sub> ] <sup>+</sup>	Av=0.239
Cl <sup>-</sup>	0.7583	Cl <sup>-</sup>	0.7623
Br <sup>-</sup>	0.7635	---	--
I <sup>-</sup>	0.7605	I <sup>-</sup>	0.7585
ClO <sub>4</sub> <sup>-</sup>	0.7392	ClO <sub>4</sub> <sup>-</sup>	0.7385
PF <sub>6</sub> <sup>-</sup>	0.7375	PF <sub>6</sub> <sup>-</sup>	0.7470

## CONCLUSION

The structural formula of the octahedral pseudo (3,2,3)-tetramine oxalato cobalt(III) and (tn)<sub>2</sub> octahedral carbonato complexes, provided strong evidences to their conducting properties due to the nature and size of their ions during migration in their solutions. Relaxation and electrophoretic properties in solution were consistent with the behaviour of these ions. The collected data revealed that  $\Lambda_0$  varied in short limited range either for oxalato or carbonato complexes. The extent of solvation of these ions, depended on the structure of coordinated amine and arrangement of the chelating ligands that were surrounded by water to form hydrogen bonds, may strengthen or weakened may created or disappeared.

The relative differences in  $\Lambda_0$  for given series of complexes with common oxalato cation as [Co(3,2,3)tetOx]<sup>+</sup> in the order of Br<sup>-</sup> > Cl<sup>-</sup> > I<sup>-</sup> > ClO<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup> while that for carbonato [Co(tn)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup> in the order I<sup>-</sup> > Cl<sup>-</sup> > ClO<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup>. Finally, the limiting transference numbers for given complexes were estimated and found that anions be decreased in the order Br<sup>-</sup> > I<sup>-</sup> > Cl<sup>-</sup> > ClO<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup> for oxalato complexes and the order I<sup>-</sup> > Cl<sup>-</sup> > ClO<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup> for carbonato complexes. Applying Gill's equation gives an indication about the presence of solvation process, the derived model from Gill's equation would be solvent separated ion pair where ion-dipole-ion forces existed between these two systems. Moderately change for K<sub>A</sub> complexes indicated no serious association between opposite ions. Accordingly, the experimental R values were found to be parallel to K<sub>A</sub> values as related to Fuoss model.

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