

Selective Solvation of Co^{2+} in Aqueous Ethanol

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Abstract- Selective solvation of Co^{2+} in aqueous ethanol has been studied by measuring visible-region spectra and changes therein upon addition of ZnCl_2 . The study is based on comparison of spectra in the mixtures with those in the individual neat solvents. Water exhibited stronger selective solvation. On increasing ethanol content absorbance due to organo-complex increased at the expense of the aquo-complex. Only the above two solvation complexes of Co^{2+} have been found to co-exist in the system. As a simple model it is suggested that Co^{2+} distribute themselves between the two types of solvation spheres. A value of 25 ± 2 has been estimated for the distribution coefficient which is defined as the concentration ratio ($c_{\text{aq}}/c_{\text{org}}$). Upon ZnCl_2 addition to the Co^{2+} solutions in ethanol-rich mixtures ($x_{\text{ethanol}} \geq 0.6$) increase of absorbance for the aquo-complex while simultaneous decrease for the organo-complex indicated more favoured formation of the aquo-complex by Co^{2+} as compared to Zn^{2+} .

Keywords- Cobalt (II) Solvates; Aqueous Ethanol; Selective Solvation; Visible-Region Spectra

I. INTRODUCTION

Liquids and their mixtures have always remained a subject of interest for various investigations regarding structure and dynamics [1, 2]. When an electrolyte is dissolved in a solvent, in the first instance local structure in the immediate vicinity of ions is disrupted but re-organization of the solvent molecules around the ions takes place to form solvation complexes or solvates [3, 4]; studies on electrolyte solutions, among others, also include investigation of the solvate structure [5, 6]. In solvent mixtures an additional subject of interest is selective solvation [7-9]; as regards the primary solvation sphere of ions in binary mixtures, following possibilities may occur: (a) only one type of solvate is formed which comprises of just one of the solvent components, (b) solvate comprising of both the components (mixed solvation spheres) is formed but their ratio in the solvate is not same as in the bulk mixture, (c) as in the (b) above but their ratio in solvate and bulk is the same and (d) solvates of both the components co-exist in equilibrium. It is only in the case of (c) above where the selective solvation does not take place [10]. The phenomenon of selective solvation occurs when molecules of the two components do not behave as equally strong ligands due to difference in their dipole moments and sizes [11].

Various techniques may be employed to investigate the solvation entities but measurement of UV-Vis spectra of transition metal electrolyte solutions are considered as useful [12-14] because such spectra are quite sensitive to change(s) occurring in the solvates. Generally spectra depend on properties of solvate, comprising of the central metal ion and ligands [15]. Regarding the ligand which is commonly the solvent molecule, its size, dipole moment, strength in the electrochemical series [16] etc. tend to affect the spectrum. Change in number and/or nature of the ligand and even its geometry around the ion should be accompanied with a corresponding variation in the spectrum. Whereas mere change of the ligand geometry may affect both intensity as well as position of the absorption peak, replacing a ligand by another is responsible for shifting the λ_{max} [17]. Therefore systematic measurement of the spectra for solutions of transition metal ions at different concentrations and mixture compositions may well be exploited to establish nature of the solvates and phenomenon of selective solvation. The spectra measured in the neat components are compared with those in their mixtures of varying compositions; any difference may plausibly be attributed to change(s) in the solvation sphere. In the present study the above scheme has been extended to indirectly monitor solvation behaviour of the cation (of a *white electrolyte*) whose solution does not absorb in the visible region; such and related information of the ion may be obtained from its effect on the spectrum due to a transition metal ion.

Aqueous alcohols are interesting solvent systems as they exhibit enhanced internal structure resulting from stronger mutual associations of the molecules [18, 19]. The present study is about $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in aqueous mixtures of ethanol and ZnCl_2 has been used as the *white electrolyte*. Both the electrolytes exhibit good solubility in aqueous ethanol with Cl^- as common ion. Co^{2+} solutions in neat ethanol and water exhibit absorption peaks at quite different positions, which can readily be employed not only to establish existence of their respective solvates but also the concentrations. Advantages of using the chlorides, besides others, are their relatively higher solubilities in aqueous alcohols and much less influence of Cl^- on solution properties like viscosity, structure formation etc. [20, 21]; hence any effect may be largely attributed to the cations. In the water-rich mixtures, Co^{2+} is selectively solvated by water as only the aquo-complexes are formed in the solution [22]. However, in the mixtures containing excess ethanol two distinct peaks, one each of the aquo- and organo-complex, are observed [23]. Upon addition to the *white electrolyte* (ZnCl_2) into Co^{2+} solution in aqueous ethanol, there can be two possibilities: either Zn^{2+} does not affect the solvation behavior of Co^{2+} hence no change in the spectrum should take place, or there is an influence which should then also be reflected in the spectrum. Zn^{2+} having rather high charge density [23] are likely to compete with Co^{2+} in the solvation process. More conveniently, this may be established in a situation where water mole fraction in the mixture is just enough not to allow organo-complex formation; now if the organo-complex peak should start appearing and get enhanced with subsequent addition of ZnCl_2 , it may be concluded that Zn^{2+} are being preferentially solvated by water compared to Co^{2+} .

II. EXPERIMENTAL

Chemicals with given purities as provided by the manufactures {ethanol > 98.0 % (BDH), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ = 98.0 % (Fluka) and ZnCl_2 = 99.0 % (BDH)} were used as such without further purification; contribution due to water from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, being negligible, was ignored. Water was re-distilled with a few crystals of KMnO_4 and a little amount of NaOH in an all-glass quickfit apparatus [24]. Mixtures were prepared by adding together weighed amounts of the two neat solvents while $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solutions of desired molarities were prepared by the standard procedure. For the effect of added *white electrolyte* on the spectra, calculated amount of ZnCl_2 was added to the known volume of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution to get the required mole ratio of the two electrolytes in the solution; in each case solutions were prepared three times for which the spectra were reproducible within 2% uncertainty. A balance, ER-180A from A & D, Japan (accuracy within ± 0.1 mg) was used for weighing and spectra were measured employing glass cells of 1 cm path length on a Shimadzu UV 120-02 single beam spectrometer whose wavelength was pre-calibrated for the λ_{max} of aqueous KMnO_4 solution at 525 nm [25]. All the samples were pre-thermostated at 25°C and the temperature was found to remain within $25 \pm 1^\circ\text{C}$ during measurement of the spectra.

III. RESULT AND DISCUSSION

Solutions of CoCl_2 in neat water exhibit only one absorption peak in the visible region at 520 nm for which the Beer law is well obeyed up to 0.20 M furnishing value of ϵ_{max} as $4.5 \text{ M}^{-1}\text{cm}^{-1}$ (Fig. 1). Similar results have been reported for cobalt (II) making octahedral complex in water for the highest wavelength transition, ${}^4T_{1g}(F) \leftarrow {}^4T_{1g}(P)$ [15, 26]. On the other hand solutions in neat ethanol obey the Beer law up to 0.025 M of CoCl_2 , furnishing ϵ_{max} value of $167 \text{ M}^{-1}\text{cm}^{-1}$ at 670 nm (Fig. 2), for the dominating ${}^4A_{2g} \leftarrow {}^4T_{1g}(P)$ transition of the tetrahedral organo-complex formed by ethanol [15, 26].

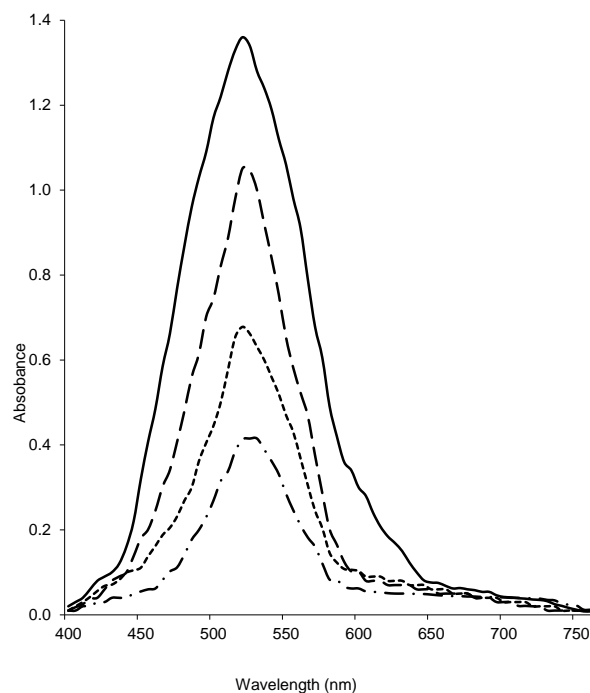


Fig. 1 Spectra of CoCl_2 solutions—0.20, 0.15, 0.10 and 0.06 M in neat water

Absorbance maxima at the two distinct wavelengths have been exploited to obtain qualitative and quantitative information on the absorbing species present in the aqueous ethanol solutions. Spectra in water-rich mixtures and even in the mixture having 50 mol % water (Fig. 3a) resemble to one in neat water indicating that water is the stronger ligand. However, slightly higher ϵ_{max} value of $5.0 \text{ M}^{-1}\text{cm}^{-1}$ may be due to distortion from the perfect octahedral symmetry of the aquo-complex in the mixture. On the other hand in the ethanol-rich mixture containing 60 mol % ethanol, presence of both aquo- and organo-complexes can be established from their respective absorption maxima at 520 and 670 nm (Fig. 4a). As the ethanol mole fraction is further increased, absorbance at 670 nm increases at the expense of that at 520 nm (Fig. 5a & Fig. 6a); formation of the aquo-complex even in the presence of 90 mole% ethanol reveals that water behaves as much stronger ligand than ethanol and that the organo-complex are only formed in the ethanol-rich mixtures. Since $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and ethanol were used without dehydrating, a small peak at 520 nm may tend to appear which has been ignored. From the unchanged positions of the absorption peaks, it may be readily concluded that the two aforementioned solvation complexes do co-exist but there is no direct indication for the formation of complexes comprising of both the solvents. Using Beer's plots to determine concentrations of the two co-existing complexes, a value of 25 ± 2 has been estimated for the "distribution coefficient", $c_{\text{aq}}/c_{\text{org}}$. Procedure employed to determine the distribution coefficient is essentially the same as described earlier [27].

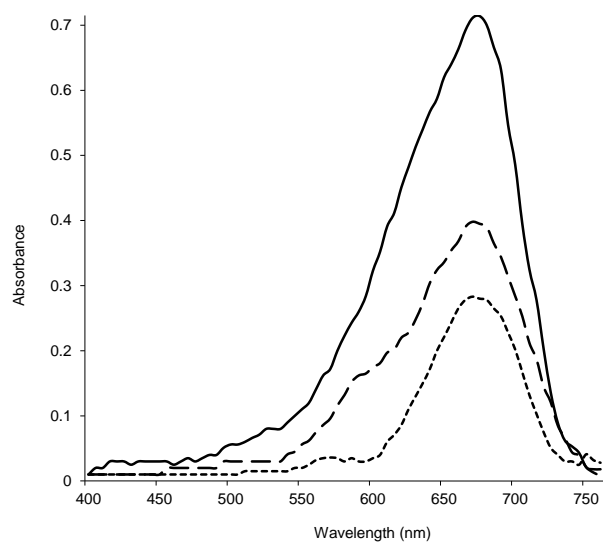


Fig. 2 Spectra of CoCl_2 solutions—0.025, 0.015 and 0.010 M in neat ethanol

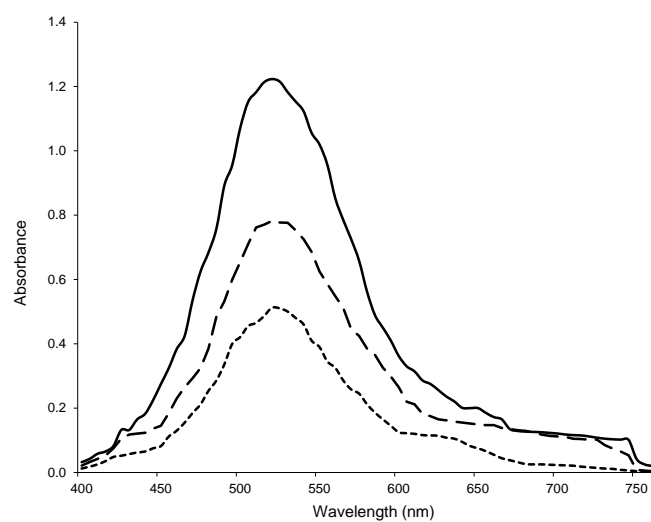


Fig. 3a Spectra of CoCl_2 solutions—0.20, 0.15 and 0.10 M in aqueous ethanol; $x_{\text{EtOH}} = 0.5$

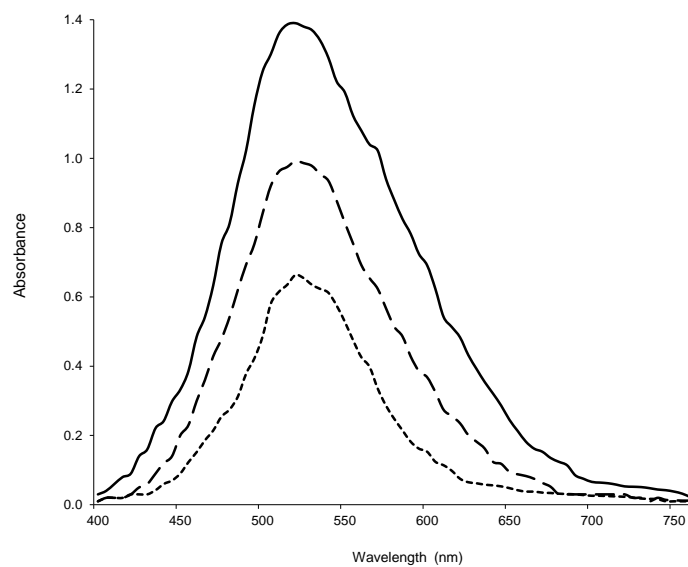


Fig. 3b Same as in Fig. 3a with equal concentrations of CoCl_2 and ZnCl_2

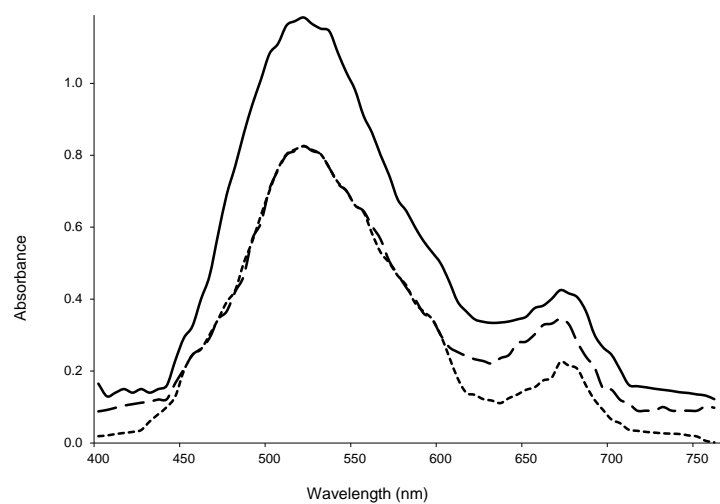


Fig. 4a Spectra of CoCl_2 solutions—0.20, 0.15 and 0.10 M in aqueous ethanol; $x_{\text{EtOH}} = 0.6$

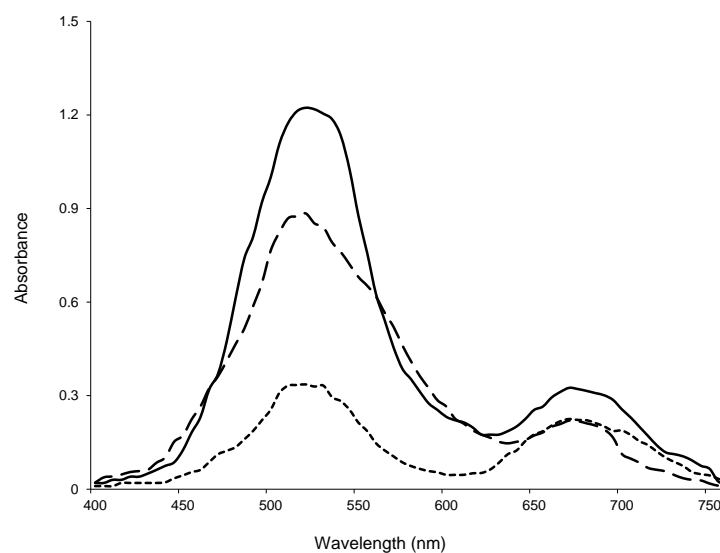


Fig. 4b Same as in Fig. 4a with equal concentrations of CoCl_2 and ZnCl_2

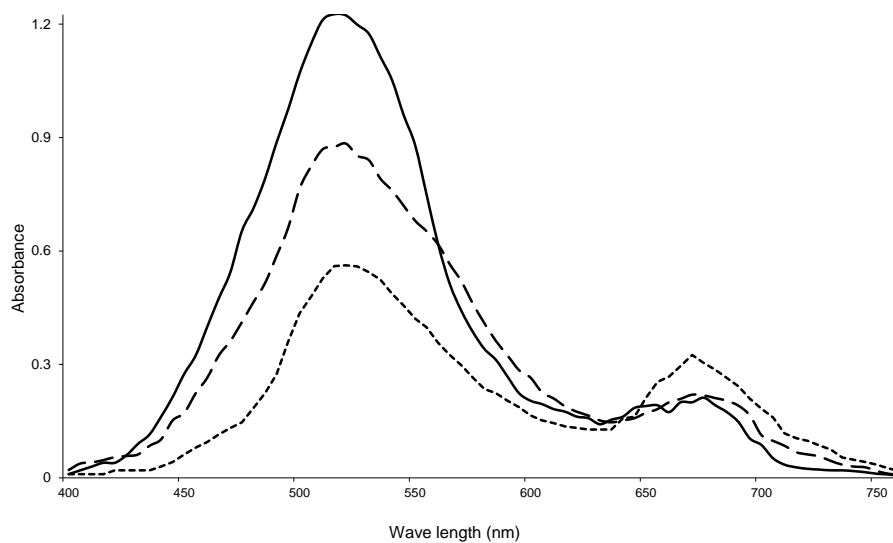


Fig. 4c Spectra of 0.15 M CoCl_2 solutions having—0.2, --- 0.15 and · · 0.1 M ZnCl_2 in aqueous ethanol of $x_{\text{EtOH}} = 0.6$

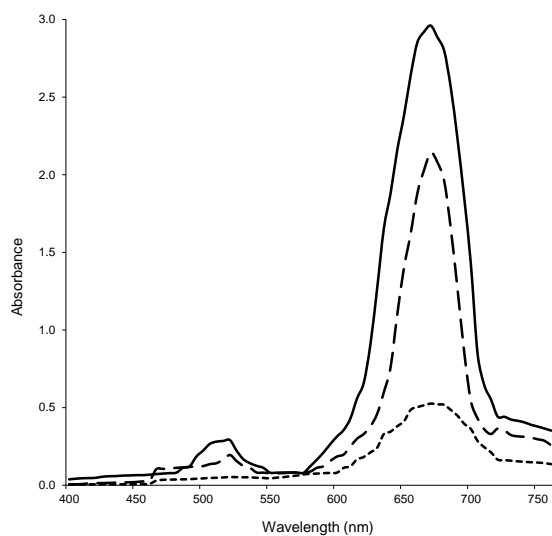


Fig. 5a Spectra of CoCl_2 solutions—0.15, 0.10 and 0.025 M in aqueous ethanol; $x_{\text{EtOH}} = 0.8$

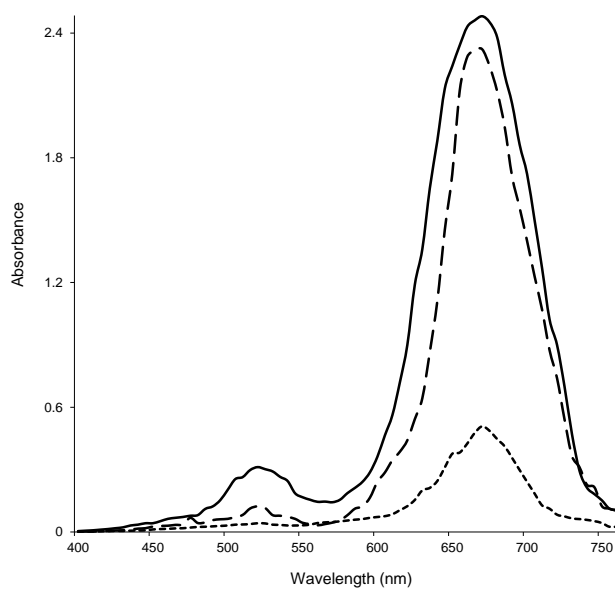


Fig. 5b Same as in Fig. 5a with equal concentrations of CoCl_2 and ZnCl_2

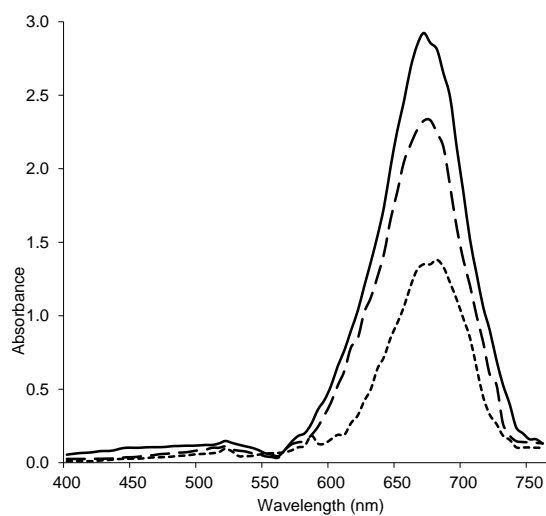


Fig. 6a Spectra of CoCl_2 solutions—0.15, 0.10 and 0.06 M in aqueous ethanol; $x_{\text{EtOH}} = 0.9$

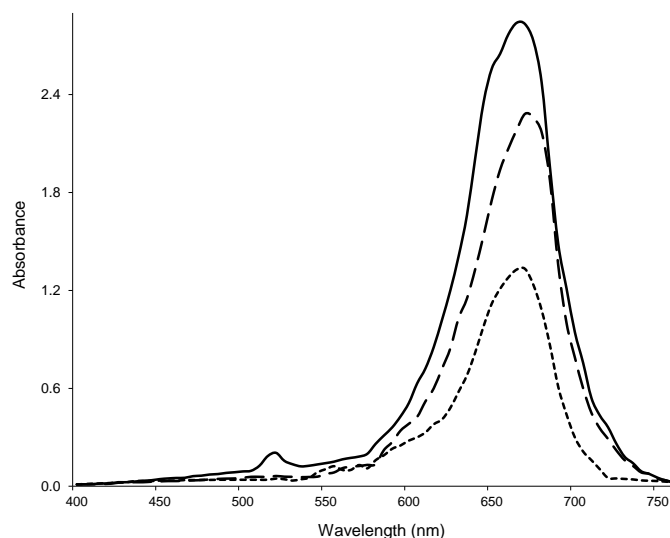


Fig. 6b Same as in Fig. 6a with equal concentrations of CoCl_2 and ZnCl_2

When same concentration of Zn^{2+} and Co^{2+} is maintained and the ethanol content in the mixture is gradually increased (x_{ethanol} from 0.5 to 0.9), consistent increase of absorbance at 520 nm is observed while that at 670 nm shows decreasing trend due to formation of the organo-complex (Figs. 3b-6b); even at the equal mole fraction of the two solvents (Fig. 3) there is an indication for existence of the organo complex of Co which upon Zn addition is not available. The above behaviors indicate that Co^{2+} , compared to Zn^{2+} , is preferentially solvated by the water molecules. This is further demonstrated in Fig. 4c where different $\text{Zn}^{2+}/\text{Co}^{2+}$ mole ratios have been maintained in the $x_{\text{ethanol}} = 0.6$ mixture; here the absorbance at 520 nm exhibits an increases with addition of more Zn^{2+} .

IV. CONCLUSION

Co^{2+} are selectively solvated by water molecules in the aqueous mixtures of ethanol. In the mixtures having excess ethanol, the organo-complex of Co^{2+} also co-exists and ratio of the two complexes, $c_{\text{aq}}/c_{\text{org}}$ is determined as 25 ± 2 . Further Co^{2+} , as compared to Zn^{2+} , are preferentially solvated by water molecules.

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