QUANTITATIVE THERMODYNAMIC EVIDENCE OF TRANSITION FROM HEXACOORDINATED TO TETRA- AND PENTACOORDINATED STRUCTURES IN AQUEOUS COPPER(II) AND ZINC(II) COMPLEXES

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A calculation method previously used in the study of simple ion pairs is extended in the present work to the entropies of formation of copper(II) and zinc(II) complexes with polydentate ligands in aqueous solution. Not only a qualitative, but also a quantitative and more significant discussion of the entropy data seems possible by this method. In particular, if the literature entropy data for copper(II) complexes with some carboxylic ligands and for zinc(II) with polyamines are used, the change from 6 to 4 in the coordination number of the cation is demonstrated, in accordance with previous suggestions. In the complex$(Zntren)^{2+}$, the metal shows a coordination number of 5, in agreement with previous X-ray results.
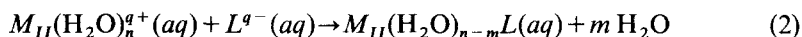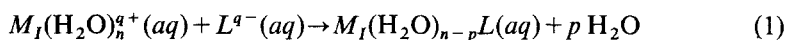
It is well known that the Irving–Williams series of stabilities of metal-ligand complexes from manganese to zinc is determined by enthalpy factors. In fact, the same order of ΔG is followed, in general, by ΔH, while no similar sequence is observed for entropy [1]. Nevertheless, the I.W. series of enthalpies is markedly different in some cases. For example, for aqueous complexes of copper(II) with ligands such as malonate, succinate or glutarate, an abnormally endothermic enthalpy of association is observed, so much so that the enthalpy sequence between copper and nickel is reversed.

The cause of these irregularities has been investigated on the basis of a simple qualitative discussion of the thermodynamic data, or in some cases by means of spectroscopic data. In particular, the inversion between nickel and copper with the above-mentioned ligands has been attributed to a strong Jahn–Teller effect for the latter cation. This effect would cause the release of an abnormally high number of water molecules from the copper ion, with a possible change from 6 to 4 in its coordination number [1, 2]. Similar considerations have been made [3, 4] for some zinc-polyamine complexes.
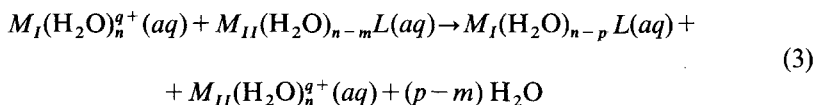
In reality, entropy data in some cases allow a more rigorous, and also a quantitative investigation of solute-solvent interactions. In this connection a previously proposed treatment should be recalled [5, 6], which was applied to simple

associations, such as those between bivalent cations and the sulfate or thiosulfate ion in aqueous medium. It was possible for these pairs to determine when they were of outer- or inner-sphere type, and in the latter case the number of water molecules displaced from the cation hydration sphere was calculated. It could be of interest to extend this treatment to more complex structures, e.g. the above-mentioned abnormal associations of copper and zinc.

This method of calculation is based, in short, on the following considerations (for greater details see refs 5, 6). Given two metal ions in aqueous solution, M_I^{q+} and M_{II}^{q+}, each of them reacting with a ligand L^{q-} to form an uncharged complex (reactions (1) and (2)), if p and m are the numbers of water molecules displaced from the first hydration sphere of the first and the second cation, respectively:

$$M_I(H_2O)_n^{q+}(aq) + L^{q-}(aq) \rightarrow M_I(H_2O)_{n-p}L(aq) + p\, H_2O \qquad (1)$$

$$M_{II}(H_2O)_n^{q+}(aq) + L^{q-}(aq) \rightarrow M_{II}(H_2O)_{n-m}L(aq) + m\, H_2O \qquad (2)$$

the corresponding ligand-exchange reaction may be considered, which is obtained from the difference between (1) and (2):

$$M_I(H_2O)_n^{q+}(aq) + M_{II}(H_2O)_{n-m}L(aq) \rightarrow M_I(H_2O)_{n-p}L(aq) +$$

$$+ M_{II}(H_2O)_n^{q+}(aq) + (p-m)\, H_2O \qquad (3)$$

ΔS_I^0 and ΔS_{II}^0 being the entropy variations for reactions (1) and (2), we obtain:

$$\Delta S_I^0 - \Delta S_{II}^0 = \overline{S'}(M_I(H_2O)_{n-p}L(aq)) - \overline{S'}(M_{II}(H_2O)_{n-m}L(aq)) +$$

$$+ \overline{S^0}(M_{II}(H_2O)_n^{q+}(aq)) - \overline{S^0}(M_I(H_2O)_n^{q+}(aq)) + (p-m)S^0(H_2O) \qquad (4)$$

where $\overline{S^0}$ is the partial molar entropy of the aqueous ion, and $\overline{S'}$ is a "corrected" partial molar entropy of the complex [7], as this value does not include the partial molar entropy of the water molecules displaced in the reaction. This contribution is given in turn by the term: $(p-m)S^0(H_2O)$.

The following observations can be made on the corrected entropy of the complex: (a) It is unaffected by the different cations in the complex if the complex is electrically neutral [5]. This is true especially in the present case, where Ni—Cu or Ni—Zn complexes are compared (see below) which contain metals of the same charge and of very similar dimensions. (b) The entropies of the different complexes are equally influenced by the ligand, L being equal for the two metals, and assuming that it has the same denticity towards them. The last condition was considered valid in all the present cases [1]. (c) In addition, the number of water molecules which constitute the first cationic hydration sphere has no influence on the entropy

of the complex, provided that this number is the same for the various metals. For the present aquo cations the same coordination number ($n = 6$) is generally assumed [8, 5]. It results from points (a), (b) and (c) above that the different corrected entropies of the two complexes are almost completely determined by the different numbers of water molecules bound to the metal ions. Taking this conclusion into account, Eq. (4) may be simplified as follows [6]:

$$\Delta S_I^0 - \Delta S_{II}^0 = \Delta S_{p-m}^0 + \overline{S^0}(M_{II}(H_2O)_n^{q+}(aq)) -$$

$$- \overline{S^0}(M_I(H_2O)_n^{q+}(aq)) \tag{5}$$

where ΔS_{p-m}^0 is the entropy variation for the displacement of $(p-m)$ water molecules from the cationic hydration sphere in exchange reaction (3). Knowing the entropy variations ΔS_I^0 and ΔS_{II}^0 for reactions (1) and (2) and the partial molar entropies of the two metal ions in aqueous solution, the value of ΔS_{p-m}^0 can be determined from Eq. (5). Finally, as the entropy variation for the displacement of 1 mole of water is known, $p-m$ can be obtained.

The literature ΔS^0 values for copper complexes with various bidentate ligands for which abnormal enthalpy values have been observed are listed in Table 1. The corresponding values for nickel have also been reported, as nickel is usually taken as reference metal ion in the discussion of the present phenomena [1]. In particular, it must be noted that normal behaviour is generally assumed for nickel with the present ligands, in the sense that it maintains a constant coordination number of 6 before and after the complex formation reaction. The ΔS^0 values used were all obtained from enthalpy values measured directly by calorimetry. Moreover, the quantities compared always referred to the same ionic strength and to $T = 25°$. The standard partial molar entropies of the metal ions are those recommended by the National Bureau of Standars [9]; they are reported in the footnote to Table 1.

Since the partial molar entropy is 9.4 cal deg^{-1} mol^{-1} for the water bound to the metal and 16.7 cal deg^{-1} mol^{-1} for free water [5, 13–15], it follows that the entropy variations for the displacement of two water moles from the metal is 14.6 cal deg^{-1}. If the above treatment is applied to the data in Table 1 for the ligand-exchange reactions between copper and nickel, a ΔS_{p-m}^0 value of 14.7 cal deg^{-1} mol^{-1} is obtained for ethylthio acetate. This value is in complete accordance with the displacement of two more water molecules from copper than from nickel. In the same way, 15.4 cal deg^{-1} mol^{-1} is obtained for glutarate. Values a little greater than expected are found for malonate and succinate, which give $p-m$ values of 2.4 and 2.5, respectively. It is difficult to ascertain whether this partial disagreement is caused by inaccuracy of the experimental data or by other disturbing factors. In any case, values are also available for the association of these two ligands with cobalt,

which is equivalent to nickel from the present point of view ($\Delta S^0 = 27.0$ and 20.7 cal deg^{-1} mol^{-1} for Co with malonate and succinate, respectively; $\bar{S}^0$ (Co, aq) $= -27.6$ cal deg^{-1} mol^{-1} [2, 9, 11]. If the mean entropy values between Co and Ni are used as reference, ΔS^0_{p-m} values of 14.5 and 15.4 cal deg^{-1} mol^{-1} are obtained for malonate and succinate, in accordance with the above hypothesis ($p - m = 2$).

As regards the possible use of the present treatment for zinc with polyamines, it must be observed that the complexes in this case are not electrically neutral (see point (a) above). However, (i) with the exception of ethylenediamine (see below) all the present ligands are at least tridentate and capable of forming strong coordinative bonds, so that the metal charge in the complex is locally neutralized and diffused over a larger structure; in other words, the various solvent-ordering abilities of the free cations (which are very similar in this case) become an almost negligible factor in the complex; and (ii) the entropy of bound water is rather high (9.4 cal deg^{-1} mol^{-1}). Hence, the conclusion can be drawn that in this case too the different "corrected" partial molar entropies of the zinc and nickel complexes examined should be mainly determined by the different numbers of water molecules bound to the metal.

The literature entropy values for complex formation of zinc and nickel with the polyamines diethylenetriamine (dien), triethylenetetramine (trien), ethylenedinamine (en) and 2,2′,2″-triaminotriethylamine (tren) are collected in Table 1 ΔS^0_{p-m} values of 14.0 and 13.0 cal deg^{-1} mol^{-1} are obtained for dien and trien, respectively, in accordance with a possible transition of zinc from the octahedral structure of the aquo cation to a tetrahedral structure in the complex [1, 21]. As

Table 1 Entropy values for the first step of association of metals with various ligands (L) and ΔS^0_{p-m} values for the corresponding ligand-exchange reaction, in aqueous solution at $T = 25°C$[a]

M_I^{2+}	M_{II}^{2+}	L	ΔS_I^0	ΔS_{II}^0	Ref.	ΔS^0_{p-m}[b]
Cu^{2+}	Ni^{2+}	(ethylthio)acetate	13.6	5.9	10	14.7
Cu^{2+}	Ni^{2+}	malonate	35.4	25.0	11	17.4
Cu^{2+}	Ni^{2+}	succinate	30.1	19.0	2	18.1
Cu^{2+}	Ni^{2+}	glutarate	18.6	10.2	12	15.4
Zn^{2+}	Ni^{2+}	dien	18.5	8.5	4	14.0
Zn^{2+}	Ni^{2+}	trien	25.0	16.0	16, 17	13.0
Zn^{2+}	Ni^{2+}	en[c]	13.1	2.9	18–21	14.2
Zn^{2+}	Ni^{2+}	tren	19.5	16.0	21	7.5

[a] The entropy values are expressed in cal deg^{-1} mol^{-1}. The thermochemical calorie is used, equal to 4.1840 J. Standard partial molar entropies of cations [9]: Cu^{2+} -23.8, Zn^{2+} -26.8, Ni^{2+} -30.8 cal deg^{-1} mol^{-1} at 25°c.

[b] Standard deviations of ΔS_I^0 and ΔS_{II}^0 only in some cases have been reported. Taking into account these values, standard deviations of ΔS^0_{p-m} ranging between 0.2 and 1.6 cal deg^{-1} mol^{-1} are obtained

[c] The values for this ligand refer to the overall reaction: $M^{2+} + 2$ en $\rightarrow (M$ en$_2)^{2+}$

regards the reaction of ethylenediamine, it must be noted that several reliable values of ΔS^0 are available in the literature, all referring to the same $T(25°)$ and $I(1.0$ mol 1^{-1}, KNO_3). Therefore, it was thought appropriate to report in the Table the mean value of these data, for both zinc and nickel. Moreover, the overall reaction for the first two steps has been considered, both for analogy with the reactions of the other polyamines (see also point (i) above), and because the transition from $n=6$ to $n=4$ for zinc with en seems to take place in the second step of association. The ΔS^0_{p-m} value of 14.2 cal deg^{-1} mol^{-1} seems to confirm exactly $(p-m=1.9)$ the proposed variation in the coordination number of zinc with en. It is interesting to note in this connection that the transition from $n=6$ to $n=4$ for the $(Zn$ en$_2)^{2+}$ complex does not appear to take place if KCl is used instead of KNO_3 as the background electrolyte [21]. Unfortunately, the present method does not seem suitable for verifying this fact, due to the possible presence of chloride ions bound to the zinc cation when KCl is used.

Finally, a possible transition from $n=6$ to $n=5$ has been previously suggested for zinc with tren, but no definitive conclusion has been drawn [1, 21]. The ΔS^0 values in Table 1 give a ΔS^0_{p-m} of 7.5 cal^{-1} mol^{-1}, in surprisingly good accordance $(p-m=1.0)$ with the above assumption. This result is also in agreement with the trigonal-bipyramidal and square-pyramidal structures $(n=5)$ previously proposed for several zinc complexes on the basis of X-ray data [22].

In conclusion, a more significant interpretation of the entropy data seems possible by the present method, particularly in the study of the structure variations in the coordination sphere of metals. The possible extension to complex formation reactions in non-aqueous media also seems interesting, with the only limit at the present time of a still scarce availability of entropy data under such experimental conditions.

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Zusammenfassung — Eine früher schon bei der Untersuchung einfacher Ionenpaare benutzte Berechnungsmethode wird auf die Entropiewerte der Bildung von Kupfer(II)- und Zink(II)-Komplexen mit Polydentat-Liganden in wässriger Lösung erweitert. Diese Methode scheint nicht nur eine qualitative, sondern auch eine quantitative und aussagekräftigere Diskussion der Entropiedaten zu ermöglichen. Ausgehend von Literaturangaben über die Entropie von Kupfer(II)-Komplexen mit einigen Carboxylgruppen enthaltenden Liganden und von Zink(II) mit Polyaminen wird, in Übereinstimmung mit früheren Annahmen, der Übergang von der 6-er in die 4-er Koordination demonstriert. Im Komplex (Zn tren)$^{2+}$ ist die Koordinationszahl des Metalls 5, in Übereinstimmung mit früheren Röntgenergebnissen.

Резюме — Метод вычисления энтропии, используемый ранее при изучении простых ионных пар, применен к случаю комплексообразования двухвалентных меди и цинка с полифункциональными лигандами в водном растворе. Метод позволяет проводить не только качественную, но и количественную интерпретацию данных энтропии. Используя литературные данные для комплексов меди с некоторыми карбоксилсодержащими лигандами и для комплексов цинка с полиаминами, показано изменение координационного числа от 6 до 4, что находится в согласии с ранними предположениями. В комплексе (Zn tren)$^{2+}$ металл проявляет координационное число 5, что согласуется с данными рентгено-структурного анализа.