

COOPERATIVE EFFECT OF  $d\pi$ -ELECTRON DELOCALIZATION IN, AND H $\cdot$ J $\cdot$   
TYPE INTERACTION OF TRANSITION METAL COMPLEXES WITH PROTIC SOLVENTS

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**Abstract** - The standard Gibbs free energies, enthalpies, and entropies of transfer of complexes of the type  $MX_nL_n$  ( $X = Cl, Br, NCS$ ;  $L =$  pyridine or substituted pyridine,  $n = 2$  or  $4$ ) between the pure amine  $L$  and amine + diluent mixtures of varying composition are discussed from the view point of solute-solvent interactions. For aprotic diluents, the free energies of transfer of complexes of a given type are, to a good approximation, independent of the nature of the central metal atom, and the solutions apparently conform to the requirements of regular solution theory. On the other hand, large specific effects are observed for protic diluents, e.g. chloroform, and these are argued to be due to the cooperative effect announced in the title. Depending on symmetry, the latter effect results in preferential stabilization by the protic solvents of centrosymmetrical octahedral complexes against those possessing other symmetries. Examples are given of stereochemical effects induced in transition metal complexes of the above type.

It is generally believed that coordination of the solvent molecules to the cation, producing well-defined solution complexes in which anions may also act as ligands, is mainly responsible for the dissolution of transition metal salts in donor solvents. More recently, specific solvation of some anions by protic solvents has also been recognized as an important factor. On the other hand, further solvation of the coordination complexes produced upon dissolution is usually disregarded when discussing the solvent effect on the solubility and ionization equilibria. In this article we intend to discuss the latter type of interactions for complexes formed by divalent transition metal salts upon dissolution in pyridine or other heterocyclic amines. The problem is pertinent to solute-solvent interactions involving coordination complexes of metal ions.

Relevant properties of the systems

The divalent transition metal chlorides, bromides, or pseudohalides dissolved in pyridine or other heterocyclic amines, as well as in mixtures thereof with non-coordinating solvents (diluents), mainly produce neutral complexes of the type  $MX_2L_n$  ( $X =$  anion,  $L =$  amine). The stoichiometries of the solid phases in equilibrium, written as  $MX_2 \cdot mL$ , may be different within some ranges of pyridine activity in the mixed solvent, depending on the nature of the system (Refs. 1-4). The solubilities are frequently in the range  $10^{-2}$ - $10^{-4}$  M, permitting ready determination of the standard Gibbs free energies of transfer of the solution complexes, by

$$\Delta G_{tr}^{\circ}(n) = RT \ln s_n^* a_L^{n-m} / s_n \quad (1)$$

where  $s_n^*$  and  $s_n$  are concentrations of the  $MX_2L_n$  complex in the saturated solution in the pure amine  $L$  and in the mixed solvent, respectively, both in equilibrium with the same solid phase  $MX_2 \cdot mL$ , and  $a_L$  is the amine activity in the mixed solvent. Alternatively, one can use the solvent-dependent activity coefficient,  $y_n^{\circ}$ , to the standard free energy of transfer related by  $\Delta G_{tr}^{\circ}(n) = RT \ln y_n^{\circ}$ , depending on convenience. Determination of either  $\Delta G_{tr}^{\circ}$  or  $y_n^{\circ}$  becomes straightforward when only a single complex occurs in the liquid phase in equilibrium with the solid compound of the same stoichiometry, and which is stable within a broad range of amine activity. Such is the case for the  $NiCl_2 \cdot py_4$  and  $ZnCl_2 \cdot py_2$  solution complexes occurring in the pyridine + diluent mixtures saturated with the respective

solid compounds. Accordingly, most of the thermodynamic transfer functions have been obtained for these two complexes which are representative of the two most common structural types. On the other hand, solution equilibria mainly of the type



are encountered in some other systems, e.g. in those involving cobalt(II) halides. Differences in the visible absorption spectra of the two complexes involved in the equilibrium may then provide the possibility of determining their separate concentrations in the saturated solutions, necessary in the calculation of the free energies of transfer (Refs. 3, 4).

#### Regularities in the free energies of transfer

For aprotic diluents, the standard free energies of transfer of complexes of the type  $\text{MX}_2\text{L}_4$ , where  $X = \text{Cl}$  or  $\text{Br}$ ,  $L = \text{pyridine}$  or  $\text{isoquinoline}$ , in a number of cases have been found to be essentially the same functions of the mixed solvent composition for different central metal atoms (Refs. 1-4). A similar regularity seems to be valid for the tetrahedral complexes  $\text{MX}_2\text{L}_2$ , but fewer experimental data have been obtained in this case (Ref. 5). The regularities prove useful in studies on solution equilibria of type (2), as well as in elucidating the nature of the solution species where other evidence is ambiguous or not readily accessible. From the point of view of the solute-solvent interactions, they may be taken as indicating essential absence of specific outer-sphere interactions in the respective systems. Accordingly, the systems might be expected to behave as regular ones, conforming to the Hildebrand-Scatchard's equation (Ref. 6).

Conformation of some non-aqueous solutions of neutral metal chelates to the model of regular solutions has earlier been claimed in connection with some practical problems of solvent extraction (Refs. 7, 8). The complex closely related to those considered here, viz.  $\text{Co}(\text{NCS})_2(\gamma\text{-pic})_4$ , was studied from this point of view by Siekierski and Narbutt (Ref. 7). A rough correlation was found between the solvent-dependent activity coefficient (derived from liquid-liquid distribution data) of the complex, on one hand, and Hildebrand's solubility parameter of the solvent, on the other, valid for a variety of aprotic solvents. At the same time, marked negative deviations from the general correlation were observed for chloroform and bromoform, the two protic solvents used in this study. These deviations were interpreted as indicating specific interactions between the complex and the solvent.

A pattern similar to that observed by Siekierski and Narbutt is observed when the free energies of transfer of the  $\text{MCl}_2\text{py}_4$  type complexes are plotted vs. the solubility parameter of the diluent (Ref. 9). Again, a rough correlation is observed for aprotic diluents, while marked deviations from the general correlation are displayed by the points corresponding to the protic diluents. However, the new observation is significant that for the latter solvents the free energies of transfer of the complexes under consideration depend markedly on the nature of the central metal atom, being more negative for  $\text{NiCl}_2\text{py}_4$  than for  $\text{MnCl}_2\text{py}_4$ . A check on a similar correlation for the  $\text{ZnCl}_2\text{py}_2$  tetrahedral complex gives less clear results. It seems that in this case both the protic as well as basic (pyridine, dioxane, ethyl acetate) solvents interact specifically with the complex.

#### Possible nature of the interactions

Siekierski and Narbutt proposed that the specific interactions between the  $\text{Co}(\text{NCS})_2(\gamma\text{-pic})_4$  complex and haloforms consisted in the  $\pi\cdots\text{H}$  type hydrogen bond formation involving the  $\gamma$ -picoline ligands (Ref. 7). In a separate study they showed that up to four chloroform molecules were consecutively bound to the complex in chlorobenzene solution, in compliance with this interpretation (Ref. 10). On the other hand, the "free" picoline was found to form two consecutive complexes under the same conditions (Ref. 11). This latter result confirmed ability of  $\gamma$ -picoline to act as a  $\pi$ -type base, since formation of the second complex can only be due to the  $\pi\cdots\text{H}$  interaction.

It seemed likely that the same type of interaction as that claimed by Siekierski and Narbutt might be responsible for the stabilizing effect

exerted by chloroform, as well as by the other protic solvents, on the  $MCl_2py_4$  type complexes, as observed in our work. However, taking into account possible  $d \rightarrow \pi^*$  electron delocalization in these complexes, as claimed by Nelson et al. (Refs. 12, 13), we are directly led to the conclusion that the two effects, if real, should be cooperative, enhancing each other. A number of important consequences might arise from this cooperation. However, the other possibility of interaction, viz. that consisting in hydrogen bond formation between the protic solvents and the coordinated chloride anions, should also be taken into consideration.

Ability of the "free" chloride anion to hydrogen bond formation with a variety of proton donors has been well established. Yet, it seems likely that it may be radically reduced upon coordination to a metal cation. In the limiting case of essentially covalent compounds such as  $GeCl_4$  or  $AsCl_3$  there seems to be no tendency for hydrogen bond formation with the haloforms, as indicated by the Hildebrand's type correlations recently studied by Siekierski et al. (Refs. 14, 15). Moreover, taking into account the now well-established ability of carbon tetrachloride and carbon tetrabromide to act as weak electron-pair acceptors (Refs. 16, 17), we should take into consideration the possibility of a similar behaviour for the chloro- or bromo-ligands in transition metal complexes. An argument against their acting as proton acceptors towards chloroform or the other protic diluents, is that this type of interaction would have to be stronger for  $MnCl_2py_4$  than for  $NiCl_2py_4$ . Being a stronger coordinating centre than manganese(II), nickel(II) should be more effective in reducing the ability of the coordinated chloride anion to act as a proton acceptor, thus resulting in a weaker interaction of its chloro-complex with chloroform compared with the analogous manganese(II) complex. The opposite is observed, as mentioned in the preceding section. On the other hand, the  $d \rightarrow \pi^*$  electron delocalization within the  $MCl_2py_4$  type complexes enhancing their  $\pi \cdots H$  type outer-sphere interaction should be more effective in this respect in  $NiCl_2py_4$  than in  $MnCl_2py_4$ , since the  $d\pi$  central metal atom orbitals are filled up in the former and only half filled in the latter. Another argument against the interaction via the coordinated chloride anions and, at the same time, in favour of the other interaction, is provided by the visible spectral effects. Unlike aprotic diluents, chloroform induces small but well detectable changes in the visible spectrum of  $NiCl_2py_4$ , corresponding to a small increase in the ligand field strength parameter,  $10 Dq$  (Ref. 9). Again, this is consistent with the expected effect of increasing  $d \rightarrow \pi^*$  electron delocalization, while an opposite effect would rather be expected if the interaction consisted in hydrogen bond formation with the coordinated chloride anions.

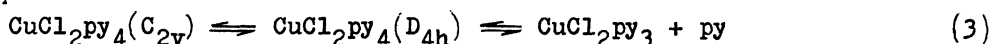
A particularly interesting possibility of obtaining a further check on the claimed cooperative effect is offered by its expected symmetry dependence. As conditions for the  $d \rightarrow \pi^*$  electron delocalization in octahedral coordination certainly are better than in any non-centrosymmetrical arrangement of ligands, the former should preferentially be stabilized by the protic solvents, provided that the effect is real. Stereochemical effects arising in this way have been found and will be described briefly below.

#### The effect of chloroform on the $CuCl_2py_n$ solution complexes

The lack of any concentration dependence of the visible absorption spectrum of copper(II) chloride dissolved in pyridine, as well as its lack of any electrical conductance, both indicate the solute is a single neutral complex,  $CuCl_2py_n$  generally believed to be tetragonally distorted octahedral (Ref. 1). However, the free energies of transfer of the complex from pyridine to pyridine + aprotic diluent mixtures of varying composition (calculated on the assumption that  $n = 4$  in eq. (1) from the solubility data of the  $CuCl_2 \cdot 2py$  solid compound) agree with those of the  $MCl_2py_4$  octahedral complexes only at low diluent contents in the mixed solvent. On the other hand, increasing deviations are observed as the diluent content increases further, and the curve becomes unacceptable for solvent compositions approaching the pure diluent. It follows that a complex of the assumed stoichiometry of  $CuCl_2py_4$  predominates in the pure pyridine solutions of  $CuCl_2$ , but it dissociates on decreasing pyridine activity to give a "lower" pyridinate. The results certainly are not fortuitous, as essentially the same patterns have been obtained for benzene, chlorobenzene, o-dichlorobenzene, toluene, and ethyl acetate playing the role of the diluents, that is for five different solvent systems for which the free energies of transfer have been mapped for a number of well - characterized octahedral and tetra-

hedral complexes (Refs. 2-4, 9, 14). In addition, similar diluent effects have been observed for solutions of copper(II) chloride in isoquinoline (Ref. 18). However, the visible absorption spectrum of copper(II) chloride does not significantly change upon aprotic diluent additions, indicating that the ligand field acting on the cupric cation likewise remains virtually unchanged.

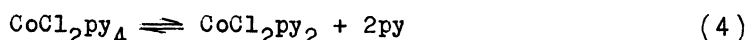
The above behaviour may readily be understood on the assumption that the  $\text{CuCl}_2\text{py}_4$  complex occurring in pyridine has an out-of-plane octahedral structure with the copper atom displaced from the central position along one of the  $\text{NCuN}$  axes (Ref. 19), a stereochemistry encountered among the solid state cupric complexes (Refs. 20-22). The non-centrosymmetrical structure of the complex is additionally supported by the relatively high intensity of the visible absorption band (at 775 nm,  $E_{\text{max}} = 141$ ) of copper(II) chloride in pyridine. However, the most striking confirmation of this claimed structure is provided by the fact that chloroform additions to pyridine induce changes in the spectrum consistent with those expected for the formation of a truly octahedral complex, viz. a gradual decrease in intensity and a concomitant blue shift of the band (to 710 nm at chloroform mole fraction of approx. 0.6). Furthermore, the spectral changes become reversed as the chloroform content in the mixed solvent increases further and a limiting spectrum similar to that in pure pyridine is attained when pure chloroform is approached. Again, this latter effect is consistent with the expected formation of the truly pentacoordinate complex at sufficiently low pyridine activities, in accordance with the equilibria scheme:



In an apparent contradiction to these inferences are the ESR spectra of the respective frozen solutions (Ref. 19), which indicate axial symmetry of the complex and coordination of four equivalent nitrogen atoms. It follows that the complex existing in the frozen solutions of  $\text{CuCl}_2$  both in pyridine and in pyridine + chloroform mixtures is  $\text{CuCl}_2\text{py}_4(\text{D}_{4h})$ . That this result does not apply to the room temperature liquid solutions, is shown by the fact that the average values of the g-factor,  $(g_{\parallel} + 2g_{\perp})/3$ , found from the frozen solution ESR spectra are markedly higher than the isotropic  $g_0$  value found at room temperature. Moreover, decreasing temperature induces changes in the visible spectrum of cupric chloride similar to those induced by chloroform additions to pyridine at the room temperature. It follows that the  $\text{CuCl}_2\text{py}_4(\text{C}_{2v})$  complex, involving an out-of-plane position of the central metal atom and a "semi-coordinated" pyridine molecule, which predominates at room temperature, is reversibly transformed into the  $\text{CuCl}_2\text{py}_4(\text{D}_{4h})$  centrosymmetrical complex upon decreasing temperature. It seems that the results may be traced back to a single model of the complex, involving three minima in the potential energy function of the metal atom along each of the two  $\text{NCuN}$  axes, the central minimum being the deepest. A gain in the configurational entropy of the complex would then be responsible for the observed acentric structure of the complex at room temperature, while additional stabilization of the central position of the cupric cation resulting from the cooperative effect of  $d_{\pi}$  electron delocalization and the H $\cdot$ J outer-sphere interaction would account for the observed effect of the protic solvent chloroform. The other systems in which similar effects are observed include:  $\text{CuCl}_2 + 4\text{-ethylpyridine} + \text{chloroform}$ ,  $\text{CuBr}_2 + \text{pyridine} + \text{chloroform}$ ,  $\text{CuCl}_2 + \text{isoquinoline} + \text{chloroform}$ .

#### The effect of chloroform on the relative stabilities of the $\text{CoCl}_2\text{py}_4$ and $\text{CoCl}_2\text{py}_2$ complexes

A solution of cobalt(II) chloride in pyridine contains two complexes,  $\text{CoCl}_2\text{py}_4$  octahedral and  $\text{CoCl}_2\text{py}_2$  tetrahedral (Ref. 18), whose relative contents may readily be determined from the visible absorption spectrum (Refs. 1, 3, 12). At room temperature and in pure pyridine the position of the equilibrium



is much in favour of the octahedral complex. On the other hand, additions of aprotic diluents to pyridine enhance formation of the tetrahedral complex in accordance with the equilibrium expression (5) owing to decreasing pyridine activity, in this case variation in the activity coefficients ratio,  $y_2^0 / y_4^0$ , being of second order importance (Ref. 3). Contrary

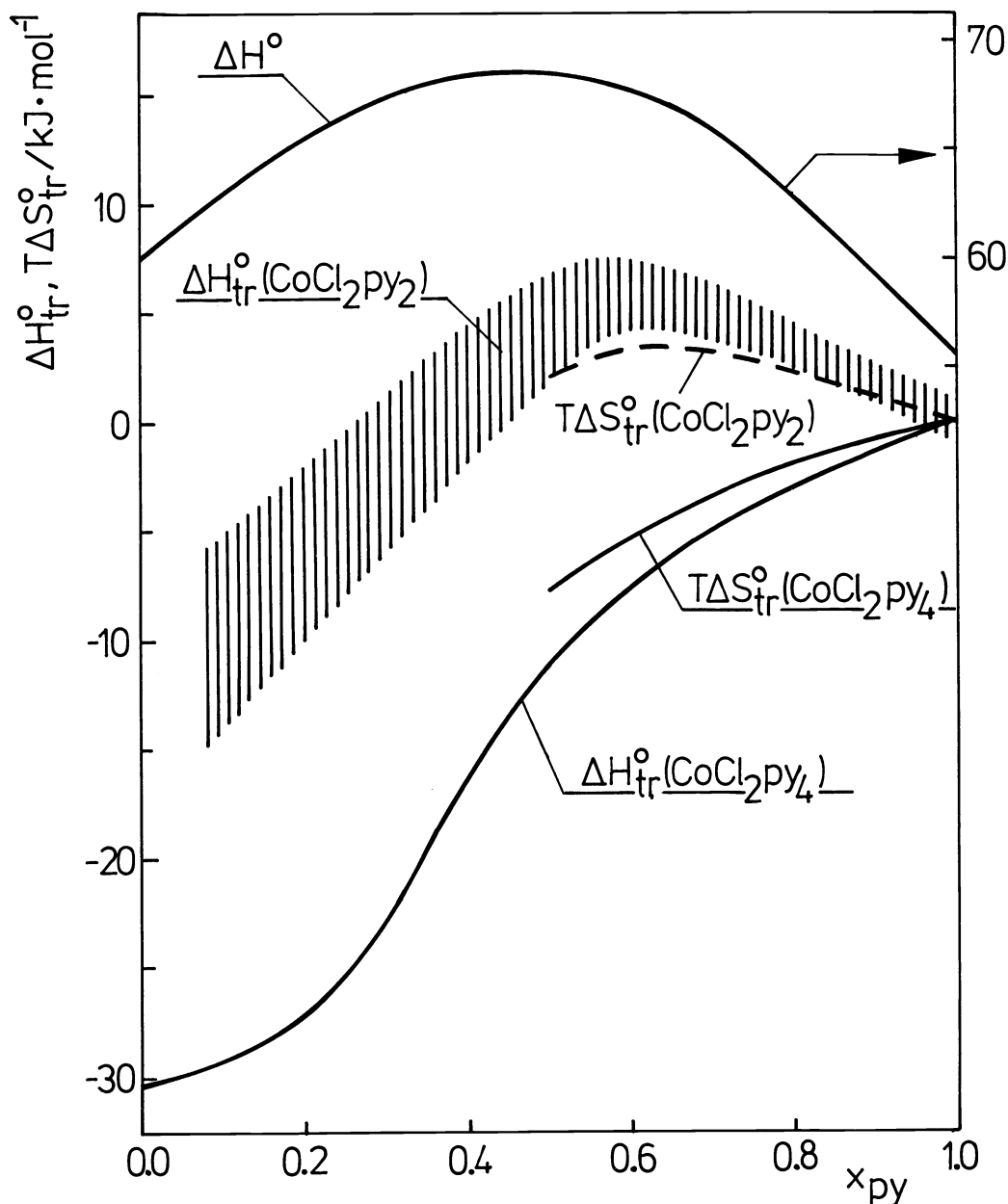


Fig. 1. The solvent composition dependences of the reaction heat,  $\Delta H^\circ$ , and the heats and entropies of transfer of two complexes involved in the configurational equilibrium (4) in pyridine - chloroform mixtures, at 25°C.

$$K^\circ = \frac{[\text{CoCl}_2\text{py}_2]}{[\text{CoCl}_2\text{py}_4]} \cdot \frac{y_2^\circ}{y_4^\circ} \cdot a_{\text{py}}^2 \quad (5)$$

to this "normal" diluent effect, additions of chloroform down to mole fraction pyridine of approx. 0.4 result in an opposite effect, despite sharply decreasing pyridine activity brought about by this protic solvent (Ref. 24). Formally, this indicates a rapid increase in  $y_2^\circ/y_4^\circ$ , outweighing decreasing pyridine activity, and thus an increase in the relative stability of the octahedral complex. Combined spectrophotometric and solubility determinations, the latter relating to the  $\text{CoCl}_2\text{py}_4$  solid compound, permit splitting the overall free energy effect into its separate contributions, viz. the free energies of transfer of the two complexes involved in equilibrium

(4), in accordance with the general relation

$$\delta(\Delta Y^0) = \Delta Y_{tr}^0(2) - \Delta Y_{tr}^0(4) + 2\Delta Y_{tr}(py) \quad (6)$$

where  $\delta$  denotes a change in the reaction function  $\Delta Y^0$  ( $Y = G, H, \text{ or } S$ ) brought about by changing solvent composition, and  $\Delta Y_{tr}^0$  are the respective transfer functions of the species indicated. It appears that increasing chloroform content in the mixed solvent brings about a marked decrease in the standard free energy of the octahedral complex and an opposite though smaller change in the standard free energy of the tetrahedral complex, as indicated by the negative and positive, respectively, free energies of transfer (Ref. 24). This observation provides a confirmation of our expectations. However, a better insight into the solvation behaviours of the two complexes involved in equilibrium (4) has been provided by a further study in which the free energy terms have been separated into their enthalpic and entropic contributions (Ref. 25). This has been possible from a combination of the reaction heats, determined at constant mixed solvent compositions from the temperature dependences of the equilibrium constants, and the calorimetric solution heats of the solid compounds, either  $\text{CoCl}_2 \cdot 4\text{py}$  or  $\text{CoCl}_2 \cdot 2\text{py}$ , using in addition the transfer heats of pyridine calculated from the heats of mixing of pyridine and chloroform reported by Becker et al. (Ref. 26). The derived thermodynamic characteristics of reaction (4) as a function of pyridine mole fraction are shown in Fig. 1. Indicated are uncertainties in the derived heats of transfer of the  $\text{CoCl}_2\text{py}_2$  tetrahedral complex arising from the rather unfavourable conditions of their determination (small relative content of the complex in the reference solution in pure pyridine). Yet, the results reveal radically different solvation behaviours of the two complexes involved in the configurational equilibrium (4). In general, the results seem to confirm the claimed nature of the interactions between chloroform and the  $\text{MCl}_2\text{py}_n$  type complexes, as the interactions appear to be much stronger for the octahedral  $\text{CoCl}_2\text{py}_4$  complex in which conditions for the  $d \rightarrow \pi^*$  electron delocalization certainly are better than in the tetrahedral complex. Yet, the heat of transfer data for the tetrahedral  $\text{CoCl}_2\text{py}_2$  complex are rather puzzling, as they indicate its ability for weaker interaction with both pyridine and chloroform. However, a better basis for a more detailed discussion of the solvation behaviours of the two types of complexes is provided by the thermodynamic transfer functions determined separately for the  $\text{NiCl}_2\text{py}_4$  and  $\text{ZnCl}_2\text{py}_2$  similar complexes, shown in a schematic way in Fig. 2. Comparison of the two Figures reveals close resemblance of the two sets of thermodynamic characteristics, thus confirming reliability of the results obtained for the experimentally more difficult cobalt(II) system.

#### Solvation of $\text{MCl}_2\text{py}_4$ and $\text{MCl}_2\text{py}_2$ type complexes

The large negative enthalpies of transfer (from pyridine to chloroform) of approx.  $-30 \text{ kJ/mol}$  for the octahedral complexes  $\text{CoCl}_2\text{py}_4$  and  $\text{NiCl}_2\text{py}_4$  directly characterize the real magnitude of changing outer-sphere interactions with changing solvent composition, while the much smaller free energies of transfer concealed large opposing enthalpic and entropic contributions. Significant is the fact that the negative enthalpies of transfer of the complexes are even slightly larger than the enthalpy of transfer of four "free" pyridine molecules from pyridine liquid to its infinitely dilute solution in chloroform. There is little doubt that the main contribution to the latter enthalpy of transfer is due to the n·H type hydrogen bond formation involving the lone electron pair on the nitrogen atom (Refs. 26, 28, 29). Once coordinated to a metal cation, the pyridine molecules may only act as  $\pi$ -type bases, and the above comparison indicates that they must have acquired additional  $\pi$ -base capacity as a result of the interaction with the metal cation. The only reasonable mechanism for this  $\pi$ -basicity enhancement seems to be the  $d \rightarrow \pi^*$  electron delocalization within the complex.

Inspection of Fig. 2 further shows that large decrease in the molar entropy accompanies transfer of the  $\text{NiCl}_2\text{py}_4$  complex from pyridine to the pyridine + chloroform mixtures, approaching  $-77 \text{ J/Kmol}$  as the pure chloroform is approached. There is little doubt, in view of all the evidence so far discussed, that the main contribution to the negative entropies of transfer is due to the consecutive outer-sphere adduct formation of the  $\text{NiCl}_2\text{py}_4$  complex with chloroform. It seems that the overall process of binding four chloroform molecules to the complex might well account for its observed

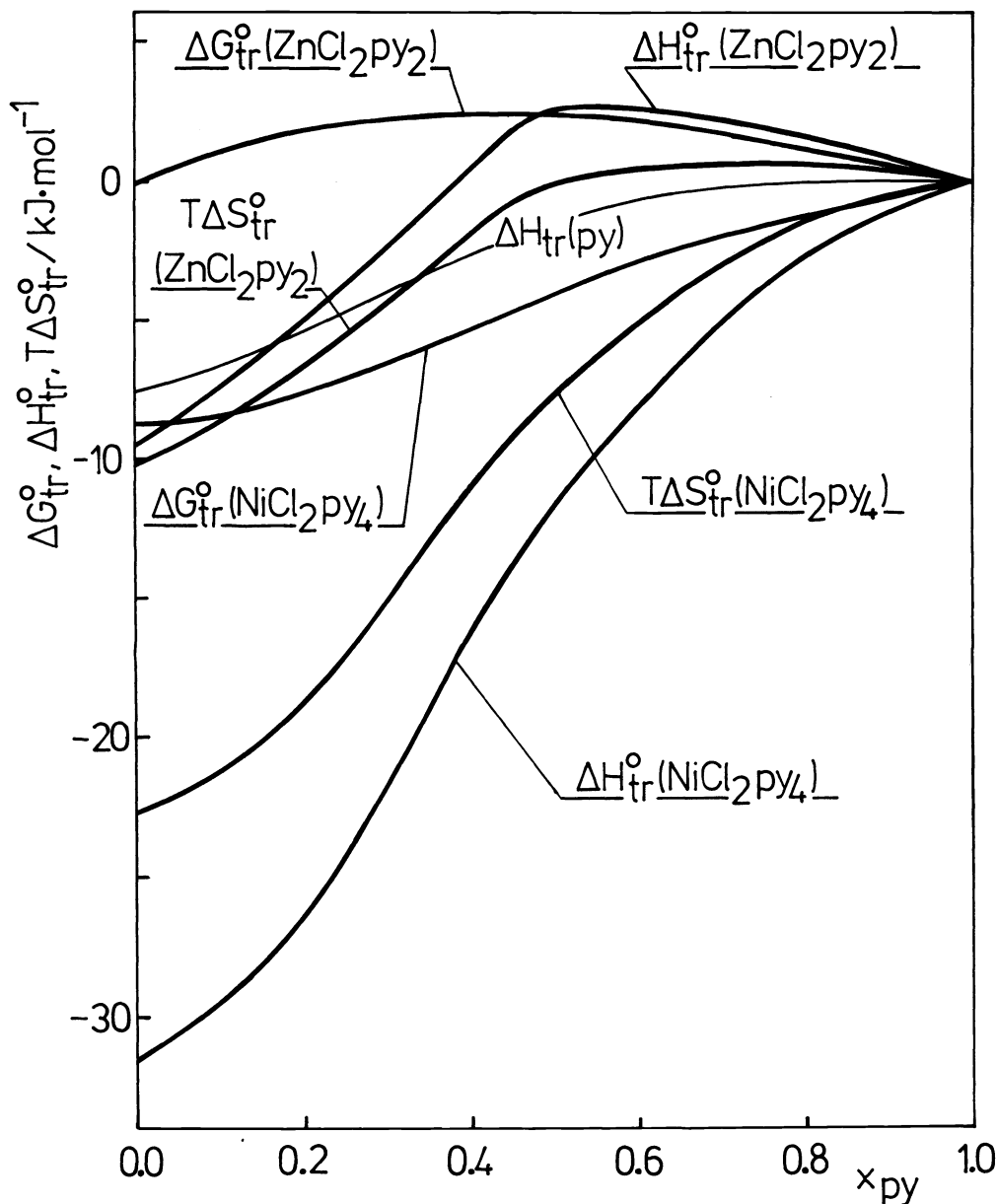


Fig. 2. The solvent composition dependences of the free energies, heats and entropies of transfer of the  $\text{NiCl}_2\text{py}_4$  and  $\text{ZnCl}_2\text{py}_2$  complexes from pyridine to pyridine - chloroform mixtures, at  $25^\circ\text{C}$ .

entropy of transfer from pyridine to chloroform. However, there may also be a contribution to the negative entropy of transfer due to the expected decrease in the rotational freedom of the pyridine ligands around the coordinative bonds, brought about by increasing  $d \rightarrow \pi^*$  electron delocalization under the influence of increasing chloroform content in the mixed solvent.

Importance of hindered rotation of the pyridine ligands in octahedral complexes, resulting from the claimed  $d \rightarrow \pi^*$  electron "back donation", in determining the over-all entropy change of reversible reactions of type (2) has first been pointed out by Nelson (Refs. 12, 13). A consistent explanation of the observed effect of the nature of the anion on the reaction entropy was proposed in terms of this basic concept. Nelson ignored solvation effects in determining the reaction entropies; this does not seem justified in the light of our present results. However, it will only be fair to say that his ideas in addition to those of Siekierski have been the starting

points in developing the present propositions.

While the entropy data for  $\text{NiCl}_2\text{py}_4$  in pyridine + chloroform mixtures do not provide direct evidence for change in the rotational contribution to the molar entropy of the complex with changing solvent composition, an indication of a possible effect of this type seems to be provided by the transfer functions determined for this complex in mixtures of pyridine with chlorobenzene (Fig. 3). A marked decrease in the molar entropy of the complex takes place in the latter system with increasing diluent content in the mixed solvent, while the heats of transfer are very small negative numbers. We tentatively ascribe the entropy changes here observed to changing internal degrees of freedom as a result of changing  $d \rightarrow \pi^*$  electron delocalization. The latter may be somewhat disfavoured by the basic solvent pyridine compared with the more neutral solvent chlorobenzene. At the same time, the small enthalpies of transfer indicate that the stabilizing effect of increasing  $d \rightarrow \pi^*$  electron delocalization may be partly counter-balanced by some other electronic effect within the complex, e.g. by increasing interaction of the  $p_\pi$  electrons of the coordinated chloride anions with the  $t_{2g}(d_\pi)$

electrons of the central metal atom. However, apart from the latter speculations, the results shown in Fig. 3 illustrate how misleading may be analyses of the free energy characteristics alone for solutions of the present type. It appears, in particular, that the behaviour of the solutions (as the regular ones) may only be due to a mutual compensation of larger enthalpic

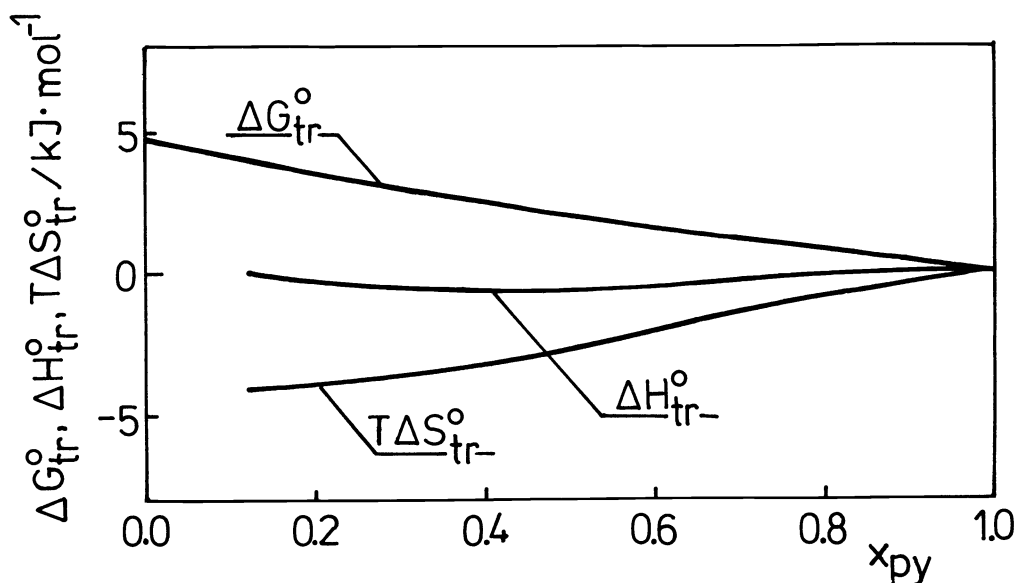


Fig. 3. The solvent composition dependences of the free energy, enthalpy, and entropy of transfer of the  $\text{NiCl}_2\text{py}_4$  complex from pyridine to pyridine - chlorobenzene mixtures, at  $25^\circ\text{C}$ .

and entropic terms. We may add that effects similar to those described above have also been observed for benzene and cyclohexane as diluents.

The other interesting feature of the results shown in Figs. 1 and 2 is the complex solvation behaviours of the tetrahedral complexes,  $\text{CoCl}_2\text{py}_2$  and  $\text{ZnCl}_2\text{py}_2$ , revealed by their separate enthalpic and entropic characteristics. As is seen, the enthalpies of transfer of the two complexes initially increase with increasing chloroform content in the mixed solvent, pass through maxima near the chloroform mole fraction of 0.5, and then decrease approaching approx.  $-10$  kJ/mol as the pure chloroform is approached. Since the 1:1 pyridine + chloroform mixture contains mainly the  $\text{CHCl}_3\cdot\text{py}$  molecular complex, neither basic nor acidic, it seems that these variations in the heats of transfer of the tetrahedral complexes indicate their specific interactions with both components of the solvent, the basic pyridine and the protic chloroform. The interactions with pyridine only slightly exceed thermal energy, thus producing quite small compensating entropy changes. On the other hand, the stronger interactions with chloroform produce drastic decrease in the molar entropies, as illustrated by the data for  $\text{ZnCl}_2\text{py}_2$ ,



which may be indicative of some reduction in the internal degrees of freedom of the complexes, in addition to the outer-sphere adduct formation.

The question arises as to the location of the basic and acidic centres in the  $MCl_2py_2$  tetrahedral complexes now under consideration. Specific interaction with chloroform via the coordinated chloride anions seems to be excluded by the fact that no essential heat of transfer effects have been observed in an auxiliary study of the related  $ZnCl_2(DMSO)_2$  complex (DMSO = dimethyl sulphoxide) on passing from a benzene rich to a chloroform rich solvent mixture containing a small amount of DMSO added. It follows that the pyridine ligands rather than the coordinated chloride anions must be responsible for the exothermic interactions with chloroform displayed by the  $MCl_2py_2$  tetrahedral complexes. The fact that the interactions are considerably weaker than those displayed by the octahedral complexes,  $MCl_2py_4$ , is consistent with the expected symmetry dependence of the  $d \rightarrow \pi^*$  electron delocalization cooperating, as suggested, with the  $\pi \cdot H$  outer-sphere interactions. As is known, proper  $d_{\pi-p_{\pi}}$  orbital overlap in regular tetrahedral symmetry is possible for both the  $e(d_{x^2-y^2}, d_{z^2})$  and  $t_2(d_{xy}, d_{xz}, d_{yz})$  central metal atom orbitals although, quantitatively, in both cases the overlaps are poorer than in octahedral symmetry in which only the  $t_{2g}$  orbitals are of the  $\pi$ -type (Ref.30). Taking the above into account we are led to the conclusion that the weaker interactions displayed by the  $MCl_2py_2$  tetrahedral complexes with pyridine must be due to the coordinated anions. This, in turn implies that the chloro-ligands acquire some electron acceptor ability as a result of their interaction with the other partners of the complex. The question requires further experimental study.

#### Some further evidence

We have been assuming so far that it is the protic properties of chloroform that are responsible for its observed specific interactions with the transition metal complexes studied. To check this assumption a number of other protic solvents have been included into study, in addition to the aprotic ones studied earlier. It has been found that additions to pyridine of strongly polar protic solvents such as water, trifluoroethanol, or n-propanol bring about ionization of the  $MCl_2py_n$  type complexes, thus precluding their study from the view point of the outer-sphere interactions. From among the protic solvents checked, 1,1',2,2'-tetrachloroethane and aniline have been selected as producing marked outer-sphere effects without changing the coordination spheres. The ability of aniline to act as a weak proton-donor has been well-established (Ref. 31), in addition to its well-characterized basic properties (Ref. 32). Despite the latter, it proves to be a much weaker coordinating agent towards nickel(II) than is pyridine.

Additions of aniline to pyridine down to pyridine mole fraction of approx. 0.3 bring about very small changes in the visible spectrum of the dissolved nickel(II) chloride, indicating persistence of the  $NiCl_2py_4$  complex occurring in the pure pyridine solution. It is only at still higher aniline contents in the mixed solvent that marked changes in the spectrum are observed, indicating exchange of the coordinated pyridine molecules for those of aniline. The limiting complex formed in the pure aniline solution of nickel(II) chloride certainly is  $NiCl_2an_4$  (an = aniline), as indicated by its visible spectrum and lacking electrical conductance. However, its attainable concentration in pyridine is very low, precluding more detailed study. On the other hand, the outer-sphere interactions of aniline with the  $NiCl_2py_4$  complex could be studied calorimetrically down to the pyridine mole fraction of 0.3, and have been found to be similar to those displayed by chloroform. On the contrary, N,N-dimethylaniline, selected for a comparative study, has been found to display behaviour typical of the aprotic diluents. The conclusion follows that the stabilizing effect exerted by aniline on the  $NiCl_2py_4$  complex, before ligand displacement becomes of importance, is due to its protic properties and probably consists in the H $\cdot\pi$  hydrogen bond formation via the pyridine ligands.

The other protic solvent studied, 1,1',2,2'-tetrachloroethane, has been found to interact less strongly than chloroform with the  $NiCl_2py_4$  complex, in accordance with its expected weaker acidity, but more strongly with the  $ZnCl_2py_2$  complex, as indicated by the respective heats of transfer. The latter extra strong interaction of tetrachloroethane with the  $ZnCl_2L_2$  type complexes disappears for 2,6-dimethylpyridine playing the role of the

neutral ligand L. These latter findings indicate that coplanarity of the two amine rings, favoured by the interaction with tetrachloroethane, is responsible for the extra-strong interactions in the respective systems. The coplanarity might, in turn, be favourable for the  $d \rightarrow \pi^*$  electron delocalization. Consideration of molecular models shows that it cannot be achieved for neighbouring pyridine molecules in the  $MCl_2py_4$  type octahedral complexes, thus explaining the "normal" solvating behaviour of tetrachloroethane towards the latter.

To obtain a further check on the importance of the  $d \rightarrow \pi^*$  electron delocalization in determining the  $\pi$ -base capacity of the coordinated pyridine molecules, that of hydrogen-bonded pyridine has been examined in the following way. The heats of transfer have been determined for the PNP.py complex (PNP = p-nitrophenol) to pyridine + chloroform mixtures of variable composition and compared with the heats of transfer of p-nitroanisole, the latter serving as a reference compound lacking the pyridine ring. It has been found that the heats of transfer of these two substances show the same variations, within experimental error, with varying composition of the mixed solvent. This result clearly indicates lacking contribution of the pyridine ring in the PNP.py complex to the observed small negative (approx. -5 kJ/mol) heat of transfer of the latter from pyridine to chloroform. In turn, this shows essential absence of the  $\pi \cdot H$  interaction of the n-hydrogen-bonded pyridine with chloroform, a conclusion apparently contradicting that of Narbutt concerning the chloroform- $\gamma$ -picoline system (Ref. 11). It seems possible, however, that pyridine hydrogen-bonded to a proton-donor weaker than p-nitrophenol may behave in a somewhat different way. Our recent heat of transfer determinations for the phenol.pyridine complex and for anisole serving as a reference compound, seem to confirm this expectation. However, the observed effect is small, radically differing in magnitude from those displayed by the  $MCl_2py_4$  type complexes.

The question of changing the nature of the anion has recently been included into our studies. The results so far obtained show that substitution of the chloride for the bromide or thiocyanate anion in the  $NiX_2py_4$  series of octahedral complexes results in the appearance of a weak interaction of the complex with pyridine, as indicated by flat maxima in the heat of transfer curves. At the same time the interaction of the complexes with chloroform remains approximately the same or even slightly increases, judging by their heats of transfer between 1:1 pyridine + chloroform mixture and the pure chloroform (19.5, 20.5, and 22.5 kJ/mol for X = Cl, Br, and NCS, respectively). The heats of transfer between pyridine and chloroform cease being indicative of the interaction of the bromo- and thiocyanato-complexes with chloroform because of the overlapping interaction with pyridine, as mentioned above. It seems that these results provide a strong support for the interaction of the complexes with chloroform via the pyridine ligands rather than via the anionic ligands whose ability to hydrogen bond formation with proton-donors should decrease in the order  $Cl^- > Br^- > NCS^-$ .

#### Concluding remarks

Solute - solvent interactions involving coordination complexes have not so far received any broader interest. The much discussed question of the solvent effect on complex formation in solution has usually been considered only from the view point of solvent molecules competing with the other ligands for the coordination sites on the central metal atom. Outer-sphere interactions of well-defined coordination complexes with the solvent medium have usually been ignored, probably being considered to be of second order importance. That this attitude may not always be justified, is shown by the stereochemical effects induced by chloroform in the solution complexes of cobalt(II) chloride and copper(II) chloride in pyridine. The author's proposition is that the latter effects may be accounted for on the assumption that the  $d \rightarrow \pi^*$  electron delocalization within the complexes cooperates with their  $\pi \cdot H$  type outer-sphere interaction with the protic solvent chloroform. The thermodynamic transfer functions determined for a number of tetrahedral and octahedral complexes in pyridine (or substituted pyridine) + diluent mixtures of variable composition have provided arguments supporting the latter concept and, at the same time, excluding possible interaction of the protic solvents with the complexes via the coordinated anions. However, indications have also been found of the ability of the complexes to some weaker interaction with pyridine, and we tentatively ascribe it to the coordinated anions. It follows that there may be more partners in the specific solute - solvent interactions involving the complexes studied. Further investigation is necessary to elucidate their intrinsic interaction producing the overall thermodynamic effects observed.

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