

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY,
TECHNICAL UNIVERSITY OF GDAŃSK, GDAŃSK, POLAND

The Relative Stability of Octahedral and Tetrahedral Complexes in Solution.

I. Chloropyridine Complexes of Divalent Transition Metals¹

BY W. LIBUŚ AND I. URUSKA

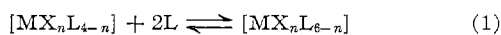
Received March 8, 1965

Solubility isotherms of MCl_2 in pyridine–chlorobenzene mixtures are reported for $M = Mn, Co, Ni, Cu,$ and Zn . It is assumed that the only equilibria existing in the saturated solutions are of the type $[MCl_2py_2] + 2py \rightleftharpoons [MCl_2py_4]$, the four-coordinate complex being tetrahedral and the six-coordinate being octahedral. Their activity coefficients are calculated in several instances from the solubility and spectrophotometric data for varying compositions of pyridine–chlorobenzene mixtures and are found to be independent of the central metal ion for a given structure of the complex. The equilibrium constants of the configuration change reactions calculated from the solubility data are reported. Their dependence on the atomic number of the central metal ion is found to be in a qualitative agreement with the expectations of the crystal field theory if an additional and probably monotonic change of the relative stability of octahedral and tetrahedral complexes within the transition series is taken into account.

Introduction

It is well known that certain predictions have been made on the basis of the crystal field theory regarding the relative stability of octahedral and tetrahedral complexes of individual transition metal ions.² These predictions are qualitatively confirmed by the present knowledge of structures encountered among transition metal complexes. However, there exist very few data that would make a quantitative verification of this theory possible.

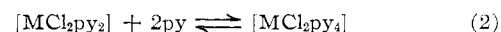
The stability of octahedral in relation to tetrahedral complexes of a metal ion with given ligands may be characterized by the magnitude of the equilibrium constant of a configuration change reaction taking place in solution. These equilibria are usually of the type



X being an anion and L a neutral ligand. In polar solvents they establish themselves in addition to the more common equilibria involving complexes of the same coordination number.³

It is obvious that the equilibrium constant of the above configuration change reaction must be dependent on the nature of the metal ion as well as on that of the ligands. A smaller effect of the medium outside the coordination spheres of complexes is probably also to be expected. Even small changes in M, X, L, or n usually result in significant changes in the magnitude of the equilibrium constant, thus practically completely shifting the equilibrium toward one or the other of the configurations involved. The result is that a systematic study of factors affecting the position of a configurational equilibrium is very difficult. Fortunately, there exists a type of equilibria that may be studied relatively easily for a broad variety of ligands and metal ions, this being $[MX_2L_2] + 2L \rightleftharpoons [MX_2L_4]$, where X is a halogenide anion and L is a neutral, monodentate

ligand. Equilibria of this type may easily be shifted in one or the other direction by changing the concentration of the neutral ligand in an inert-solvent medium, in which the configuration equilibrium establishes itself. A well-known example is represented by the equilibrium $[CoCl_2py_2] + 2py \rightleftharpoons [CoCl_2py_4]$ studied by Rohde and Vogt,⁴ by Katzin,⁵ and recently by Nelson and his collaborators.⁶ In Nelson's papers the investigation of the same type of configuration equilibria was extended to other cobalt(II) and nickel(II) complexes. In the present work the investigation of the equilibrium



has been undertaken with regard to several divalent transition metals. In the case of cobalt(II) it may easily be studied by means of absorption spectra measurements. In the case of other metals the solubilities and/or their light absorption are insufficient for a spectrophotometric study. In these cases a method based on solubility measurements proved to be applicable, and results obtained in this way will be described below. Chlorobenzene was used as an inert solvent, providing a medium for establishing the configuration equilibria.

Experimental Section

Compounds.—All metal complexes used in this work, except $MnCl_2py_4$, were prepared by methods described in the literature.⁷ They were analyzed for the corresponding metal by titration with Na_2EDTA and for chlorine by gravimetric methods. $MnCl_2py_4$ was prepared by the action of an excess of pyridine on the solid $MnCl_2py_2$. The unstable complex, in the form of white crystals, was filtered off quickly and dried between two sheets of filter paper.

Solvents.—Chlorobenzene was carefully purified by standard methods⁸ and, subsequently, fractionated through a column of ca. 30 theoretical plates. Pyridine, which was of reagent quality, was fractionated as above.

(1) Presented at the 8th International Conference on Coordination Chemistry, Vienna, Sept. 1964.

(2)(a) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952); (b) J. Bjerrum and C. K. Jørgensen, *Rec. trav. chim.*, **75**, 658 (1956).

(3) W. Libuś, "Proceedings of the Symposium Held at Wrocław, June 1962," Pergamon Press, Inc., New York, N. Y., 1964, pp. 537–550.

(4) I. Rohde and E. Vogt, *Z. physik. Chem. (Leipzig)*, **B32**, 353 (1932).

(5) L. I. Katzin, *J. Chem. Phys.*, **35**, 467 (1961).

(6) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(7) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

(8) A. Weissberger, "Organic Solvents," Interscience Publishers, Inc., New York, N. Y., 1955, p. 408.

Determination of Solubility. Equilibration.—Supersaturated solutions were first obtained by shaking the solid compound under investigation with the solvent (pyridine–chlorobenzene mixture) of a given initial composition during a period of ca. 8 hr., at a temperature 10° higher (if the solubility increased on increasing temperature) or 10° lower (if the temperature effect was reversed) than the final one required. The vessels (glass vials with ground-glass stoppers) were then placed in a thermostat and left for at least 24 hr. The equilibrated and clear solutions were taken off by means of a heated syringe from over the deposited solids and analyzed as below. The compositions of solid phases in equilibrium with the corresponding saturated solutions were determined in preliminary experiments for every metal chloride at several solvent compositions. The complex which was stable in equilibrium with the solvent of a given composition was then used in final measurements.

Analytical Procedures.—Depending on the magnitude of the concentration to be determined two methods were used. For concentrations of the metal in solution $>5 \times 10^{-4} M$ the analyses were performed by titration with $0.01 M Na_2EDTA$ by standard procedures.⁹ The solutions during the titration were heterogeneous chlorobenzene–water mixtures. In order to speed up the extraction of the determined metal to the water phase, hydrochloric acid was added and subsequently neutralized to obtain the proper value of pH. Trace concentrations of Cu(II), Mn(II), and Ni(II) were determined spectrophotometrically in the form of diethyldithiocarbamates. The methods described in the literature¹⁰ were modified in that alcohol was used as solvent. The optical density was measured at $436 m\mu$ in the case of Cu(II), at $505 m\mu$ in the case of Mn(II), and at $385 m\mu$ in the case of Ni(II). The concentrations were found from calibration curves.

Absorption Spectra.—A Zeiss VSU1 spectrophotometer equipped with a thermostated cell compartment and stoppered silica cells was used.

Results

(1) **Phase Equilibria in Systems: MCl_2 –Pyridine–Chlorobenzene.**—The dependences of the solubilities of the investigated metal chlorides on the composition of pyridine–chlorobenzene mixtures are shown in Figures 1 and 2. In the case of Mn(II), Co(II), and Ni(II), at temperatures between 20 and 30° , the solid phases in equilibrium with the saturated solutions in pyridine have the composition MCl_2py_4 . The solubility of these solids decreases with the decreasing concentration of pyridine in the solvent. In each of these three cases the composition of the solid phase in equilibrium with the solution becomes MCl_2py_2 below a certain pyridine concentration. Its solubility decreases again on decreasing pyridine concentration until a limiting value is attained at $X_{py} \rightarrow 0$. Theoretically, for a solid complex of composition MCl_2py_2 to be stable in equilibrium with a solution in chlorobenzene a definite concentration of free pyridine is necessary. This was proved to be very low in all of the cases investigated. It is only in the case of cobalt(II) that a lower solid pyridinate, *viz.*, $CoCl_2py$ (dark blue crystals), was found to form under the condition of very low pyridine activity. As the solubility of this solid in chlorobenzene is unmeasurably low, the part of the solubility isotherm corresponding to it has not been studied.

The systems involving $ZnCl_2$ and $CuCl_2$ display a

(9) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Inc., New York, N. Y., 1958, pp. 149, 217, 237, 242, 230.

(10) IUPAC, "Spectrophotometric Data for Colorimetric Analysis," Butterworth and Co. Ltd., London, 1963, pp. 151, 333, 393.

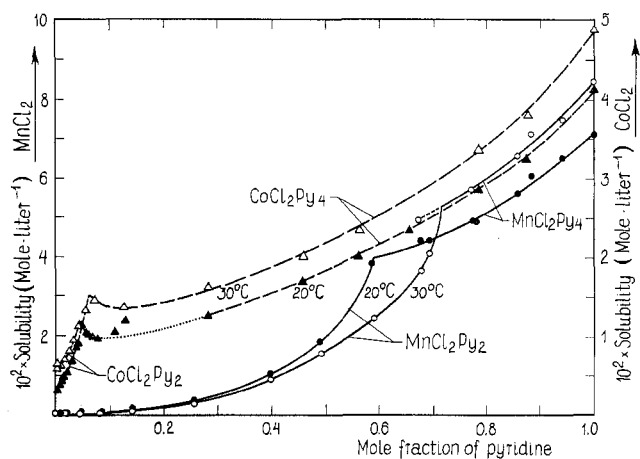


Figure 1.—Solubility isotherms of $MnCl_2$ and $CoCl_2$ in pyridine–chlorobenzene mixtures.

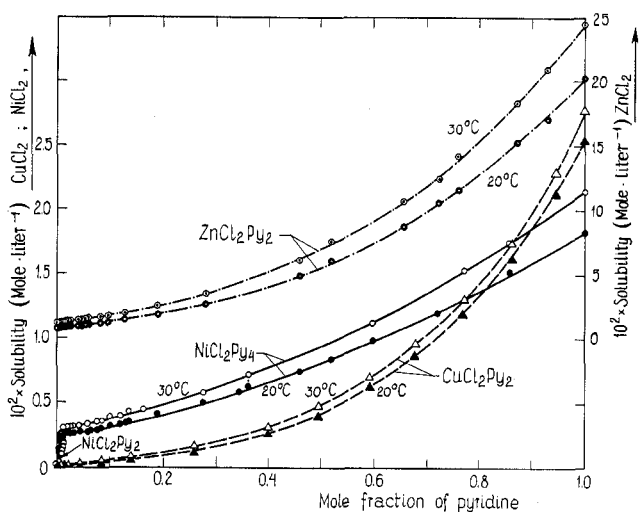


Figure 2.—Solubility isotherms of $NiCl_2$, $CuCl_2$, and $ZnCl_2$ in pyridine–chlorobenzene mixtures.

different behavior in that the solid phases have the composition MCl_2py_2 regardless of pyridine concentration in the mixed solvent. The solubility of these solids increases monotonically with increasing pyridine concentration.

(2) **Structures of Complexes in the Saturated Solutions. Solutions of $CoCl_2$.**—A solution of $CoCl_2$ in pyridine is electrically nonconducting and, at room temperature, exhibits a low-intensity absorption band at $515 m\mu$, which is characteristic of octahedral cobalt(II) complexes. On increasing temperature, the solutions turn blue, this color change resulting from another absorption band between 550 and $700 m\mu$.⁵ Similar changes of the spectrum are observed when the activity of pyridine in solution is decreased by dilution with an inert solvent.⁶ Both effects were interpreted in terms of equilibrium 2. It might be expected on this basis that the same equilibrium would be established in the solutions investigated in the present work. The absorption spectra of saturated solutions of $CoCl_2$ in pyridine–chlorobenzene mixtures of varying composition are shown in Figure 3. The composite absorption band between 550 and $700 m\mu$, with the absorption maxima at 576 , 608 , and $638 m\mu$ characteris-

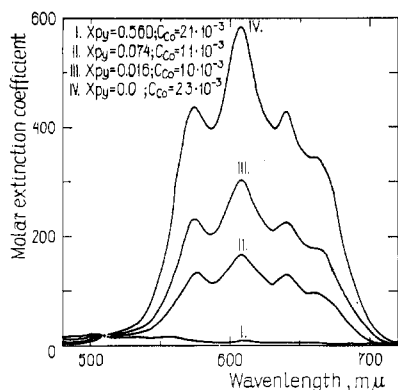


Figure 3.—Absorption spectra of CoCl_2 in pyridine-chlorobenzene mixtures.

tic of tetrahedrally coordinated cobalt(II), remains unchanged in shape and position while increasing in intensity with the decrease of the concentration of pyridine. It follows that only one tetrahedral cobalt(II) complex is present in these solutions, and it must be $[\text{CoCl}_2\text{py}_2]$ as the solutions are nonconducting.¹¹ The observation of an isosbestic point at $505 \text{ m}\mu$ indicates that there exists one octahedral complex as well.

On the basis of the assumed equilibrium 2 it is obvious that, partly at least, the increase in solubility of $\text{CoCl}_2\text{-py}_2$ on increasing pyridine concentration is due to the formation of the $[\text{CoCl}_2\text{py}_4]$ complex in solution, the activity of $[\text{CoCl}_2\text{py}_2]$ remaining constant throughout the concentration range corresponding to the solid CoCl_2py_2 in equilibrium with the saturated solution. Another reason for the increasing solubility of both solids, *viz.*, CoCl_2py_2 and CoCl_2py_4 , with increasing pyridine concentration is changes in the free energies of solvation of individual solution complexes.

Solutions of NiCl_2 and MnCl_2 .—The fact that the solubility isotherms of NiCl_2 and MnCl_2 are similar to those of CoCl_2 (Figures 1 and 2) strongly suggests that the changes which take place in solution and are responsible for solubility changes are common for them and consist in shifting the configuration equilibrium 2, M being Mn, Ni, or Co, respectively. The very strong tendency of nickel(II) to form octahedral complexes manifests itself in the steepest increase of the solubility of NiCl_2py_2 on increasing pyridine concentration. An essential difference between CoCl_2py_2 , on one hand, and MnCl_2py_2 and NiCl_2py_2 , on the other, consists in much lower solubilities of the latter two compounds in pure chlorobenzene. This may be due to essential differences in crystal lattice energies. It follows from the very low solubilities of NiCl_2py_2 and MnCl_2py_2 in pure chlorobenzene (of the order of $10^{-5} M$) that the concentrations of the four-coordinate monomeric species, *viz.*, $[\text{NiCl}_2\text{py}_2]$ or $[\text{MnCl}_2\text{py}_2]$, must, in their saturated solutions in pyridine-chlorobenzene mixtures, also be low since their activities must remain constant. Nearly all of the metal in these solutions should, therefore, be in the form of the six-coordinate complexes $[\text{MCl}_2\text{-}$

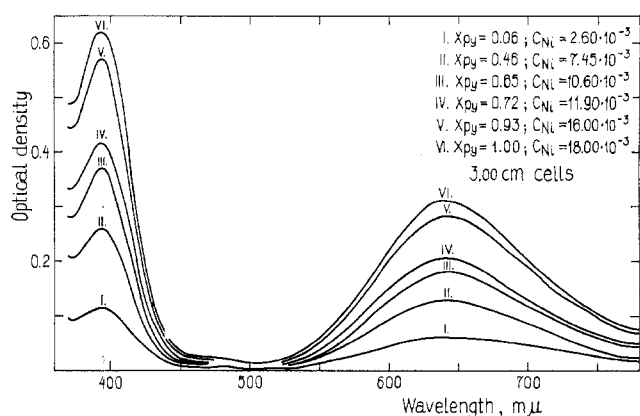


Figure 4.—Absorption spectra of NiCl_2 in pyridine-chlorobenzene mixtures.

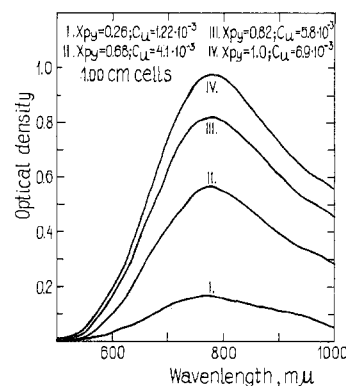


Figure 5.—Absorption spectra of CuCl_2 in pyridine-chlorobenzene mixtures.

$\text{py}_4]$. In the case of nickel(II) this conclusion is proved by the absorption spectra of the saturated solutions shown in Figure 4. The observed absorption bands at 394 and $640 \text{ m}\mu$ are characteristic of octahedral nickel(II) complexes and do not change in position and intensity (ϵ_{max} 11.5 at $394 \text{ m}\mu$ and 5.6 at $640 \text{ m}\mu$) throughout the whole composition range of the pyridine-chlorobenzene mixtures. On the other hand, no definite conclusion as to the structure of the four-coordinate complex $[\text{NiCl}_2\text{py}_2]$ may be drawn, its concentrations being too low for any absorption bands to be detectable.

As the visible absorption bands of manganese(II) complexes are spin-forbidden and are thus very weak, the spectra of MnCl_2 solutions under investigation could not be measured. Nevertheless, it is rather obvious that the six-coordinate $[\text{MnCl}_2\text{py}_4]$ solution complex will be octahedral and the four-coordinate $[\text{MnCl}_2\text{py}_2]$ will be tetrahedral, these being the symmetries expected for the high-spin electron configuration $3d^5$. An argument proving the existence of the octahedral complex $[\text{MnCl}_2\text{py}_4]$ in solution will be given in the next section.

Solutions of CuCl_2 .—The spectra of CuCl_2 solutions in pyridine-chlorobenzene mixtures (Figure 5) reveal the existence of only one copper(II) complex in the whole composition range of the mixed solvent. The position (λ_{max} $780 \text{ m}\mu$) and intensity (ϵ_{max} 141.5) of the observed absorption band are characteristic of octahedral copper(II) complexes; neither changes with the

(11) In the present paper the formulas of complexes in solution with definite compositions of coordination spheres are given in brackets, whereas unbracketed formulas are used for solid complex compounds.

changing solvent composition, thus proving the prevailing existence of the $[\text{CuCl}_2\text{py}_4]$ octahedral complex, probably with a considerable tetragonal distortion according to the Jahn-Teller effect. As the composition of the solid phase in equilibrium with the saturated solution is CuCl_2py_2 , the conclusion may be drawn that equilibrium 2 in solution must be strongly shifted to the right.

Solutions of ZnCl_2 .—These solutions do not exhibit any electronic absorption bands. The solubility of ZnCl_2py_2 (this being the only solid phase existing in equilibrium with pyridine-chlorobenzene solutions at room temperature) on passing from pure chlorobenzene to pure pyridine increases from 9.1×10^{-8} to $203 \times 10^{-8} M$ at 20° , the relative increase being much smaller than that found in the other systems so far discussed. Nevertheless, this increase might be considered as resulting from the formation of some quantities of the six-coordinate complex $[\text{ZnCl}_2\text{py}_4]$, while the concentration of the latter never reaches the critical value necessary for the formation of a solid phase of the same composition. The calculation of activity coefficients of individual tetrahedral and octahedral solution complexes, to be described in the next section, leads to the conclusion that there is little probability that this might occur. It is assumed on this basis that the $[\text{ZnCl}_2\text{py}_2]$ tetrahedral complex is the only one present in solutions of ZnCl_2 in pyridine-chlorobenzene mixtures.

(3) **Activity Coefficients.**—The dependence of the activity coefficients of the individual $[\text{MCl}_2\text{py}_2]$ and $[\text{MCl}_2\text{py}_4]$ complexes on the solvent composition must be known before determining the configuration equilibrium constants. The determination of this dependence from solubility data proved possible in several cases and will be described below.

As the reference states for the activity coefficients γ_4 and γ_6 of $[\text{MCl}_2\text{py}_2]$ and $[\text{MCl}_2\text{py}_4]$ complexes, respectively, the infinitely dilute solutions in pure chlorobenzene are assumed. The activity coefficients γ_4^* and γ_6^* defined by assuming infinitely dilute solutions of the corresponding complexes in the binary solvent of the same composition as the corresponding reference states are related to γ_4 and γ_6 by $\gamma_4 = \gamma_4^0/\gamma_4^*$ and $\gamma_6 = \gamma_6^0/\gamma_6^*$. Here γ_4^0 and γ_6^0 are activity coefficients of the complexes in infinitely dilute solutions in the binary solvent normalized against infinitely dilute solutions in chlorobenzene. (Activity coefficients of infinitely dilute solutions of the complexes in the mixed solvents normalized against the corresponding solutions in pyridine, which will also be used, will be denoted by γ_4^\bullet and γ_6^\bullet .) Owing to the very low solubilities of the investigated complexes in pyridine-chlorobenzene mixtures, it may be assumed that $\gamma_6^* = 1$ and $\gamma_4^* = 1$. Thus, we have $\gamma_4 = \gamma_4^0$ and $\gamma_6 = \gamma_6^0$, which means that the activity coefficients of the individual complexes in the solutions under investigation are assumed to be determined solely by the composition of the solvent. The six-coordinate $[\text{MCl}_2\text{py}_4]$ complexes will be considered first.

$[\text{NiCl}_2\text{py}_4]$.—As shown in the preceding section,

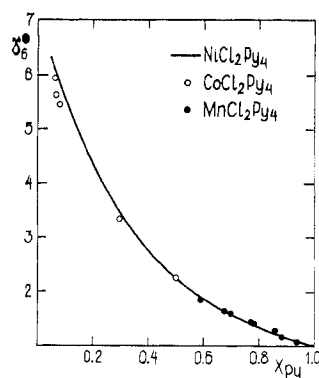


Figure 6.—The dependence of the activity coefficients γ_6^\bullet of $[\text{MCl}_2\text{py}_4]$ complexes on the mole fraction of pyridine in pyridine-chlorobenzene mixtures.

the concentration of the four-coordinate complex $[\text{NiCl}_2\text{py}_2]$ in the saturated solutions of NiCl_2py_4 in pyridine-chlorobenzene mixtures is extremely small. It may be assumed, therefore, that $s_6 = c_6^s$, s_6 denoting the solubility of NiCl_2py_4 and c_6^s the concentration of the six-coordinate complex $[\text{NiCl}_2\text{py}_4]$ in the saturated solution. As the activity of $[\text{NiCl}_2\text{py}_4]$ must remain constant in all solutions equilibrated with the solid of the same composition we shall have

$$\gamma_6^\bullet s_6 = s_6^\bullet \quad (3)$$

where s_6^\bullet is the solubility of NiCl_2py_4 in pure pyridine. Making use of this relation, the activity coefficient γ_6^\bullet of $[\text{NiCl}_2\text{py}_4]$ has been calculated for the pyridine content changing from $X_{\text{py}} = 0.01$ to $X_{\text{py}} = 1$. Its dependence on X_{py} is shown in Figure 6 by the continuous line.

$[\text{MnCl}_2\text{py}_4]$.—The relations with manganese are analogous to those for nickel, in that the solutions equilibrated with the solid MnCl_2py_4 contain only minute concentrations of the four-coordinate complex. The activity coefficient of $[\text{MnCl}_2\text{py}_4]$ could, therefore, be calculated from an equation analogous to eq. 3. The resulting values are plotted in Figure 6 (dark circles) and may be seen to be very close to the corresponding values found for $[\text{NiCl}_2\text{py}_4]$.

$[\text{CoCl}_2\text{py}_4]$.—The solutions saturated with the solid CoCl_2py_4 contain comparable quantities of both $[\text{CoCl}_2\text{py}_2]$ and $[\text{CoCl}_2\text{py}_4]$ complexes, the activity of the latter being constant. The concentrations of $[\text{CoCl}_2\text{py}_2]$ in the saturated solutions may be determined spectrophotometrically. The required value of ϵ_4 for this complex at $610 \text{ m}\mu$ has been found in the way described in section 4. Considering that in solutions equilibrated with solid CoCl_2py_4 , the activity of the solution complex of the same composition must be constant, we have

$$\gamma_6^\bullet c_6^s = c_6^{s^\bullet} \quad (4)$$

where c_6^s is the concentration of $[\text{CoCl}_2\text{py}_4]$ in a saturated solution of a given solvent composition and $c_6^{s^\bullet}$ is its concentration in the saturated solution in pyridine. The resulting values of γ_6^\bullet for $[\text{CoCl}_2\text{py}_4]$ are denoted in Figure 6 by open circles. These values are less pre-

TABLE I

ACTIVITY COEFFICIENTS γ_4^0 AND γ_6^0 OF $[\text{ZnCl}_2\text{py}_2]$ AND $[\text{NiCl}_2\text{py}_4]$, RESPECTIVELY, IN PYRIDINE-CHLOROBENZENE MIXTURES AT 20°

X_{py}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
γ_4^0	0.66	0.46	0.32	0.23	0.17	0.12	0.09	0.07	0.06	0.045
γ_6^0	0.85	0.65	0.52	0.41	0.34	0.28	0.24	0.20	0.17	0.15

cise than those determined for $[\text{NiCl}_2\text{py}_4]$ and $[\text{MnCl}_2\text{py}_4]$ as a result of high optical densities of the saturated solutions in question. Nevertheless, they follow sufficiently closely the curve common for the other two.

On the basis of the above-described experimental results, the following generalization may be formulated. The dependence of the activity coefficients γ_6 on the composition of a binary solvent is the same for all octahedral complexes of the type $[\text{MCl}_2\text{py}_4]$ regardless of the central metal ion, the latter belonging to the first transition series. This regularity is not surprising as the interaction between a complex of a given structure (including the nature of the ligands) with the medium outside the coordination sphere may be expected to be independent of the central metal ion provided there is no possibility of stronger interactions, such as the hydrogen-bond formation.

$[\text{CoCl}_2\text{py}_2]$.—In all solutions saturated with the solid CoCl_2py_2 the activity $\gamma_4^0 c_4^s$ of the complex $[\text{CoCl}_2\text{py}_2]$ must be constant, from which it follows that

$$\gamma_4^0 c_4^s = c_4^{s_0} \quad (5)$$

where c_4^s is the concentration of $[\text{CoCl}_2\text{py}_2]$ in the saturated solution of CoCl_2py_2 in pure chlorobenzene. Although a saturated solution of CoCl_2py_2 in pure chlorobenzene is in a metastable equilibrium (the solid phase being CoCl_2py), its concentration (see Table II) may easily be determined by extrapolation or even directly, as the deposition of the solid CoCl_2py takes place very slowly. It is clear from the analysis of the absorption spectra that $[\text{CoCl}_2\text{py}_2]$ is the only complex present in these solutions. It may be assumed on this basis that $c_4^{s_0} = s_4^0$. The concentration, c_4^s , of $[\text{CoCl}_2\text{py}_2]$ in saturated solutions at various compositions of the solvent was determined spectrophotometrically using the value of ϵ_4 found by extrapolation from Figure 10 (see the next section). The values of γ_4^0 found in this way are plotted in Figure 7 (circles).

$[\text{ZnCl}_2\text{py}_2]$.—Phase equilibria in the system involving ZnCl_2 have been discussed in section 2. The

TABLE II
SOLUBILITIES OF CHLOROPYRIDINE COMPLEXES AND CONFIGURATION EQUILIBRIUM CONSTANTS

Metal ion	Temp., °C.	Solubility, M , and composition of solid phase		K_x
		In chlorobenzene from extrapol.	In pyridine	
Mn(II)	20	$1.2 (\pm 0.2) \times 10^{-5}$ MnCl ₂ py ₂	$70.7 (\pm 0.5) \times 10^{-3}$ MnCl ₂ py ₄	$2.7 (\pm 0.6) \times 10^3$
	30	$1.2 (\pm 0.2) \times 10^{-5}$ MnCl ₂ py ₂	$84.5 (\pm 0.5) \times 10^{-3}$ MnCl ₂ py ₄	$2.0 (\pm 0.3) \times 10^3$
Co(II)	20	$3.5 (\pm 0.1) \times 10^{-3}$ CoCl ₂ py ₂	$39.8 (\pm 0.5) \times 10^{-3}$ CoCl ₂ py ₄	$8.3 (\pm 0.2) \times 10^2$
	30	$5.9 (\pm 0.1) \times 10^{-3}$ CoCl ₂ py ₂	$48.9 (\pm 0.5) \times 10^{-3}$ CoCl ₂ py ₄	$3.5 (\pm 0.1) \times 10^2$
Ni(II)	20	$7 (\pm 6) \times 10^{-6}$ NiCl ₂ py ₂	$18.1 (\pm 0.5) \times 10^{-3}$ NiCl ₂ py ₄	$5.9 (\pm 5) \times 10^6$
	30	$7 (\pm 7) \times 10^{-6}$ NiCl ₂ py ₂	$21.5 (\pm 0.5) \times 10^{-3}$ NiCl ₂ py ₄	$2.7 (\pm 2.4) \times 10^6$
Cu(II)	20	$1.7 (\pm 0.3) \times 10^{-5}$ CuCl ₂ py ₂	$25.5 (\pm 0.5) \times 10^{-3}$ CuCl ₂ py ₂	$9.8 (\pm 1.4) \times 10^2$
	30	$4.8 (\pm 0.3) \times 10^{-5}$ CuCl ₂ py ₂	$27.8 (\pm 0.5) \times 10^{-3}$ CuCl ₂ py ₂	$4.4 (\pm 0.6) \times 10^2$
Zn(II)	20	$9.1 (\pm 0.3) \times 10^{-3}$ ZnCl ₂ py ₂	$203 (\pm 0.5) \times 10^{-3}$ ZnCl ₂ py ₂	<0.1
	30	$12 (\pm 0.3) \times 10^{-3}$ ZnCl ₂ py ₂	$245 (\pm 0.5) \times 10^{-3}$ ZnCl ₂ py ₂	<0.1

For calculation purposes of the present paper we are primarily interested in activity coefficients γ_6^0 rather than in γ_6^* . The calculation of γ_6^0 from the determined values of γ_6^* is possible owing to the fact that the solubility, s_6^0 , of NiCl_2py_4 in pure chlorobenzene may easily be found by an extrapolation of the experimentally determined curve (Figure 2) to $X_{\text{py}} = 0$. In this way we find that $s_6^0 = 2.8 \times 10^{-3} M$ for NiCl_2py_4 in chlorobenzene. Considering eq. 3 and $\gamma_6^0 = s_6^0/s_6$, we find that $\gamma_6^0 = s_6^0\gamma_6^*/s_6 = 0.15\gamma_6^*$. The values of γ_6^0 found in this way for NiCl_2py_4 are listed in Table I for varying compositions of the solvent.

Activity coefficients γ_4^0 of tetrahedral complexes $[\text{MCl}_2\text{py}_2]$ could be determined in two instances which follow.

25-fold increase in the solubility of ZnCl_2py_2 on passing from chlorobenzene to pyridine would correspond to a change in the solvation energy of $[\text{ZnCl}_2\text{py}_2]$ equal to 1.9 kcal./mole between these two solvents if it were the only zinc(II) complex present in solution. This seems to be quite plausible, and we may try to calculate γ_4^0 assuming that $c_4^s = s_4$. Under this assumption we have

$$\gamma_4^0 s_4 = s_4^0 \quad (6)$$

the notations being analogous to that used previously. The results of these calculations are shown in Figure 7 by the full line. It may be seen that within the limits of solvent composition where γ_4^0 of $[\text{CoCl}_2\text{py}_2]$ has been determined, there is essentially the same dependence of the activity coefficient of the two complexes on sol-

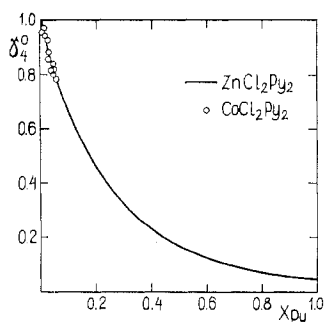


Figure 7.—The dependence of the activity coefficients γ_4^0 of $[MCl_2py_2]$ complexes on the mole fraction of pyridine in pyridine-chlorobenzene mixtures.

vent composition. The following conclusions may be drawn from this coincidence: (1) the underlying assumption of the essential absence of $[ZnCl_2py_4]$ in solutions of $ZnCl_2py_2$ in chlorobenzene-pyridine mixtures is true, and (2) the dependence of the activity coefficients γ_4^0 of tetrahedral complexes $[MCl_2py_2]$ on the composition of the solvent is the same for different transition metals. Numerical values of γ_4^0 found for $[ZnCl_2py_2]$ from a large-scale diagram for various compositions of pyridine chlorobenzene mixtures are quoted in Table I together with the values of γ_6^0 for $[NiCl_2py_4]$.

(4) **The Determination of the Configuration Equilibrium Constants from Solubility Data.**—For calculation purposes we define the configuration equilibrium constant by the relation

$$\frac{c_6\gamma_6}{c_4\gamma_4X_{py}^2\gamma_{py}^2} = K_x \quad (7)$$

X_{py} being the mole fraction of free pyridine, γ_{py} its rational activity coefficient, c_6 and c_4 the equilibrium concentrations (M) of the six-coordinate and four-coordinate complexes, respectively. As a reference state for γ_{py} we assume an infinitely dilute solution of pyridine in chlorobenzene in the absence of the dissolved complex, γ_{py} being unity under these conditions. Taking into account that the concentrations c_4 and c_6 of the metal complexes are always very small, we may assume that γ_{py} depends only on the solvent composition and is unaffected by the presence of dissolved complexes.

Assuming, as was done in sections 2 and 3, that the only forms of metal chlorides in pyridine-chlorobenzene mixtures are the complexes $[MCl_2py_2]$ and $[MCl_2py_4]$, we have

$$s_4 = c_4^s + c_6^s \quad (8)$$

for any solution saturated with the solid MCl_2py_2 . Under a further assumption that in a solution of MCl_2py_2 in pure chlorobenzene all of the metal should be present in the form of $[MCl_2py_2]$, we have $c_4^s = s_4^0/\gamma_4^0$, which together with (7) and (8) leads to the equation

$$s_4\gamma_4^0 = s_4^0 + s_4^0K_xX_{py}^2\frac{\gamma_4^0}{\gamma_6^0} \quad (9)$$

provided that $\gamma_{py} = 1$ for solutions of low pyridine concentration ($X_{py} < 0.1$). This equation may form

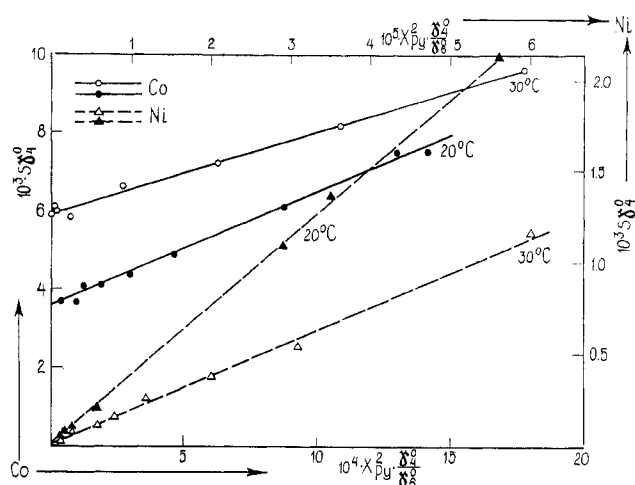


Figure 8.—Determination of K_x for cobalt(II) and nickel(II) according to eq. 9.

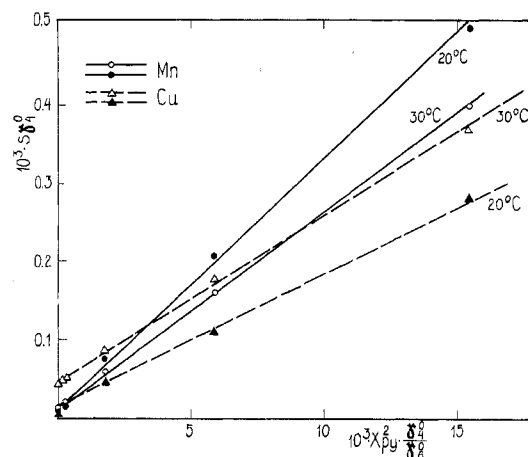


Figure 9.—Determination of K_x for manganese(II) and copper(II) according to eq. 9.

the basis for a graphical evaluation of the configuration equilibrium constants, K_x , from solubility measurements, provided that the variations of γ_4^0 and γ_6^0 with solvent composition are known. Assuming that they are identical for all complexes of the corresponding structure irrespective of the central metal ion, the values found for $[ZnCl_2py_2]$ and $[NiCl_2py_4]$ have been used in further calculations.

Figures 8 and 9 show the plots of the products $s_4\gamma_4^0$ against $X_{py}^2\gamma_4^0/\gamma_6^0$ which, according to eq. 9, should be linear. The lines drawn have been calculated by the method of least squares. It is worth stressing in this place that the experimental points follow the straight lines very closely, thus providing the validity of the underlying assumption, according to which, in all of the systems investigated, the only equilibrium in solution is the one given by eq. 2.

The resulting values of the configuration equilibrium constants are quoted in Table II together with the solubilities of the complexes indicated in the pure solvents.

The configuration equilibrium constant, K_x , as defined by eq. 7 has been used in the present section because it may be expected that the rational activity

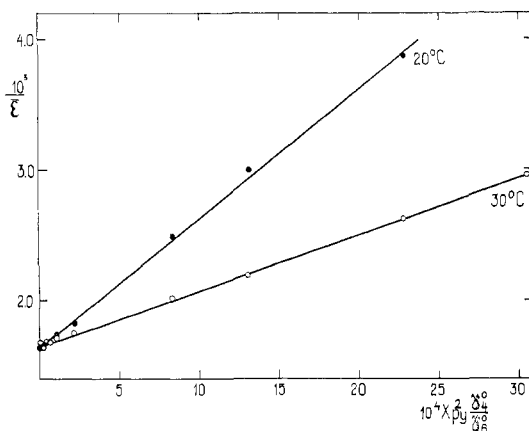


Figure 10.—Determination of K_x for cobalt(II) according to eq. 11.

coefficient of pyridine, γ_{py} , will be constant and equal 1 in a broader concentration range than the practical one, γ_{cpy} , derived from molar concentration would be. To recalculate K_x into the common form of the equilibrium constant defined by

$$K = \frac{c_6 \gamma_6}{c_4 \gamma_4 c_{py}^2 \gamma_{cpy}^2} \quad (10)$$

the relation $K = 0.0104K_x$ may be used (valid at 20°). Both K_x and K are thermodynamic equilibrium constants referring to the reaction taking place in chlorobenzene solution. For Zn(II) the upper limit of K_x was estimated to be 0.1. This value arises from an estimation, based on a discussion of activity coefficients presented in section 3, that in a solution of $ZnCl_2$ in pyridine at least 90% of the total zinc(II) is present in the form of $[ZnCl_2py_2]$.

The reliability of the solubility method could be verified by spectrophotometric measurements in the case of cobalt(II). Inserting $c_4 = c\bar{\epsilon}/\epsilon_4$ and $c_6 = c - c\bar{\epsilon}/\epsilon_4$ ($\bar{\epsilon}$ is the average molar extinction coefficient of cobalt(II), c is its total concentration, and ϵ_4 is the molar extinction coefficient of $[CoCl_2py_2]$) into eq. 7, we obtain after rearrangement

$$\frac{1}{\bar{\epsilon}} = \frac{1}{\epsilon_4} + \frac{K}{\epsilon_4} X_{py}^2 \frac{\gamma_4^0}{\gamma_6^0} \quad (11)$$

This equation is valid for the spectral region where $[CoCl_2py_2]$ is the only light-absorbing species derived under the same assumptions with regard to the activity coefficients as in the solubility method. The plot of $1/\bar{\epsilon}$ against $X_{py}^2 \gamma_4^0 / \gamma_6^0$ is shown in Figure 10. From the intercept we find $\epsilon_4 = 608$ at $610 \mu\mu$. This value of ϵ_4 has been used in calculations of activity coefficients of $[CoCl_2py_2]$ and $[CoCl_2py_4]$ complexes described in section 3. The value of K_x for cobalt(II) found from Figure 10 is $6.0 (\pm 0.3) \times 10^2$ at 20° and $2.5 (\pm 0.1) \times 10^2$ at 30°. The calculated confidence limits of K_x do not account for the observed differences between the results obtained by the spectrophotometric and solubility (Table II) methods, thus indicating the existence of some systematic error. It seems very probable that the formation of the solid $CoCl_2py$ at lowest pyridine

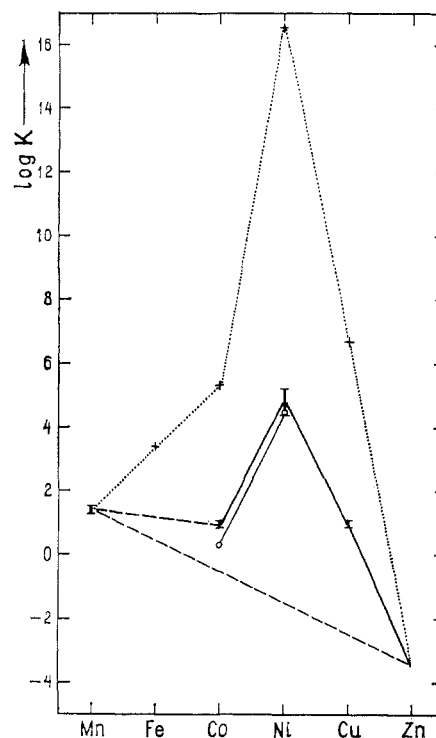


Figure 11.—The dependence of $\log K$ on the atomic number of the central metal ion.

concentrations in the solvent may be responsible for some uncertainty involved in the solubility method in the case of cobalt(II). Fortunately, no such interfering effect was observed with the other systems investigated.

Discussion

Although the equilibrium constants have been determined in this work at two temperatures (20 and 30°), their precision is not sufficient for a reliable calculation of the corresponding enthalpy changes. The solubility relations will, presumably, be more favorable in the case of bromo- and thiocyanatopyridine complexes, and it is hoped that for these systems more precise values of equilibrium constants will be obtained. Fortunately, it seems very probable that the entropy change of the configuration change reaction 2 will not vary significantly on passing from one metal ion to another in the series involved. Thus, changes in ΔH° of the configurational equilibrium 2 should be approximately parallel to changes in ΔG° , which themselves are proportional to $\log K$.

The plot of $\log K$ (K being defined by eq. 10) against the atomic number of the central metal ion is shown in Figure 11. Before any discussion of this curve will be given, a brief comment as to the meaning of K is necessary. As determined in the present work, the values of K represent the relative stability of the six-coordinate $[MCl_2py_4]$ and the four-coordinate $[MCl_2py_2]$ complexes in chlorobenzene solution. It is less obvious that they represent the relative stabilities of octahedral and tetrahedral complexes of these compositions. Taking into account the discussion presented in the preceding sections, it may be assumed that the octahedral structure

(regular or distorted) of all the six-coordinate complexes involved has been proved experimentally in addition to being the only reasonable one. The relations are less clear as regards the four-coordinate complexes $[MCl_2py_2]$. The tetrahedral structure was proved directly in the case of $[CoCl_2py_2]$ and, on the basis of a discussion regarding activity coefficients, was found to be very probable in the case of $[ZnCl_2py_2]$. In addition, this structure of $[MCl_2py_2]$ in the case of manganese(II) and zinc(II) seems to be the only reasonable one in view of their electronic configuration and their known stereochemical properties. On the other hand, in the case of nickel(II) and copper(II) there exists the possibility that the four-coordinate complexes $[MCl_2py_2]$ may be either tetrahedral (most probably distorted, according to Jahn-Teller effect) or planar.

An argument in favor of the tetrahedral structure in the case of $[NiCl_2py_2]$ is found when comparing our results with those of Nelson and Shepherd,¹² who determined the equilibrium constant for the reaction $[MI_2py_2] + 2py \rightleftharpoons [MI_2py_4]$ in benzene solution for $M = Co$ and Ni . Their values have been plotted in Figure 11 in addition to our results relating to the equilibrium represented by eq. 2. It may be seen that the increase in $\log K$ on passing from Co to Ni is nearly the same for these two types of configurational equilibria. As the tetrahedral structure of $[NiI_2py_2]$ has been proved spectroscopically, it becomes very probable that the structure of $[NiCl_2py_2]$ is also tetrahedral. If this complex were planar, the increase in $\log K$ on passing from Co to Ni would probably have to be smaller than that found in this work. In addition to the above arguments, the tetrahedral structure of both $[NiCl_2py_2]$ and $[CuCl_2py_2]$ solution complexes becomes more probable than the planar one on the basis of a correlation of the experimental results with the predictions of the crystal field theory, to be discussed further.

Summing up the above discussion, it may be assumed that the curve shown in Figure 11 represents the variation of the relative stability of octahedral and tetrahedral complexes involved in equilibrium 2 with the atomic number of the central metal ion within the second half of the first transition series. Several features of this variation, as represented in Figure 11, find a qualitative confirmation in the information relating to the formation of tetrahedral halogeno complexes of divalent transition metals in water solutions. Thus, it appears that the formation of $[CoCl_4]^{2-}$ takes place at about the same concentration of $LiCl$ or HCl ¹³ as does the formation of tetrahedral chloro complexes of copper(II).¹⁴ These facts are consistent with nearly the same value of K of reaction 2 found for $Co(II)$ and $Cu(II)$. In addition, it is known that zinc(II) forms $[ZnCl_4]^{2-}$ tetrahedral complexes in water solution readily,¹⁵ whereas nickel(II) does not. These facts also remain in

a qualitative agreement with the curve shown in Figure 11.

Blake and Cotton¹⁶ have recently determined and discussed the enthalpies of the reaction $R_2MCl_4(s) + \infty H_2O = [M(H_2O)_6]^{2+} + 2R^+ + 4Cl^-(\text{solution})$ for $M = Mn, Fe, Co, Ni, Cu,$ and Zn , where $R = (C_6H_5)_3CH_3As^+$. The dependence of $\log K$ on the atomic number shown in Figure 11 is very similar to the variation of $\Delta H_M - \Delta H_{Mn}$ for the above reaction found in their work. This coincidence, together with the facts mentioned above, strongly suggests that the dependence of the relative stability of octahedral and tetrahedral complexes of divalent transition metals in solution on their atomic number as characterized by Figure 11 has a general validity. Of course, this generalization does not contradict the known fact that symmetry of complexes in solution depends critically on the nature of the ligands.

On the basis of the experimental curve shown in Figure 11 it seems possible to draw certain conclusions regarding the nature of factors determining the relative stability of octahedral and tetrahedral complexes in solution on the atomic number of the central metal ion. The fact that the value of K of equilibrium 2 is much higher with manganese(II) ($K = 27$ at 20°) than with zinc(II) ($K < 10^{-3}$) is most significant for speculations of this type. Since the crystal field stabilization is not operating with these two ions, it may be concluded that this effect is not the only reason for the differences between individual transition metals with regard to their stereochemical properties in solution. This rather obvious conclusion is in agreement with the opinion represented by Katzin⁵ in his discussion of factors determining the structure of complexes. However, on the other hand, the decrease in $\log K$ on passing from Mn to Zn may suggest that in the absence of the crystal field stabilization effects there would be a continuous decrease in the relative stability of octahedral and tetrahedral complexes along the transition series, while the above effects might be responsible for the "irregularities" observed. This opinion has in essence already been formulated by Nelson and Shepherd¹² and may be considered a special case of a more general formulation by Gill and Nyholm¹⁷ and by Blake and Cotton.¹⁶ A rigorous examination of this supposition seems to be impossible in view of serious difficulties, mostly theoretical, in finding the actual values of CFSE for individual complexes. In addition, the absorption spectra of the four-coordinate complexes $[MCl_2py_2]$ involved in equilibrium 2 cannot, except those of $[CoCl_2py_2]$, be measured owing to their very low concentrations. Under these circumstances the only reasonable procedure seemed to be the simplest and very approximate calculation of the differences in CFSE of the octahedral and tetrahedral complexes involved in the investigated equilibria. It consisted in the assumption that $10Dq = 10,000 \text{ cm.}^{-1}$ for all octahedral $[MCl_2py_4]$ complexes, this being about the mean of the

(12) S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, in press.

(13) W. Libuś, *Roczniki Chem.*, **35**, 411 (1961); **36**, 999 (1962).

(14) W. Libuś and H. Jędrzejczak, unpublished results.

(15) (a) M. L. Delwaille, *et al.*, *Compt. rend.*, **206**, 187 (1938); (b) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 137 (1948).

(16) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **3**, 5 (1964).

(17) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

values estimated by other authors¹⁵ for the complexes $[\text{CoCl}_2\text{py}_4]$, $[\text{NiCl}_2\text{py}_4]$, and $[\text{CuCl}_2\text{py}_4]$. For tetrahedral $[\text{MCl}_2\text{py}_2]$ complexes four-ninths of the above value of the splitting has been assumed. In addition, the strong field limit stabilization factor has been used in every case.

In order to examine the applicability of the simple scheme, the crystal field stabilization effects superimposed on the above-mentioned continuous decrease of the relative stability of octahedral and tetrahedral complexes, we shall start from the assumption that $\log K$ would vary linearly with Z between Mn and Zn in the hypothetical absence of the crystal field stabilization. For this we need a definite value of K for Zn, while in the present work only its upper limit has been estimated (10^{-3}). As it happens, just this order of magnitude of K for Zn is to be expected if we assume that the decrease in ΔH° of reaction 2 on passing from Mn to Zn is approximately the same as that found by Blake and Cotton¹⁶ for the reaction $\text{R}_4\text{MCl}_4(\text{s}) + \infty \text{H}_2\text{O} = \text{solution}$. This seems to be quite reasonable, and we estimate that $\log K = \text{ca. } 3.5$ for Zn. The addition of the differences in CFSE values of octahedral and tetrahedral complexes to the corresponding straight-line values results in a curve shown by the dotted line in Figure 11. It may be seen that the shape of this curve is remarkably similar to the experimental although the calculated values of $\log K$ are much higher than the experimental ones. Alternatively, the differences in CFSE between octahedral and tetrahedral complexes for the metals involved may be found from the experimental curve in Figure 11 assuming that the dependence of $\log K$ on the atomic number of the metal would vary linearly between Mn(II) and Zn(II) in the absence of the crystal field effects. It will be seen that the "experimental" values found in this way would be about three times smaller

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than those calculated on the basis of the simple crystal field model.

It follows from the above discussion that the crystal field stabilization effects, when considered as superimposed on a continuous decrease of the relative stability of octahedral complexes along the first transition series, allow for a qualitatively satisfactory explanation of the differences between individual metal ions with respect to their tendency to form octahedral and tetrahedral complexes in solution.¹⁹

List of Symbols

c_4, c_5	Equilibrium concentrations of the complexes $[\text{MCl}_2\text{py}_2]$ and $[\text{MCl}_2\text{py}_4]$, respectively
c_4^s, c_6^s	As above, in saturated solutions
s_4, s_5	Solubilities of the solids MCl_2py_2 and MCl_2py_4 , respectively
s	Solubility of MCl_2 , regardless of the composition of the solid phase ²⁰
γ_4, γ_5	The activity coefficients of $[\text{MCl}_2\text{py}_2]$ and $[\text{MCl}_2\text{py}_4]$ solution complexes, respectively; reference state: infinitely dilute solution in chlorobenzene
γ_4^*, γ_6^*	As above; reference state: infinitely dilute solution in the mixed solvent of a given composition
γ_4^0, γ_6^0	Activity coefficients of $[\text{MCl}_2\text{py}_2]$ and $[\text{MCl}_2\text{py}_4]$ complexes in an infinitely dilute solution in a mixed solvent; reference state: infinitely dilute solution in chlorobenzene
$\gamma_4^\bullet, \gamma_6^\bullet$	As above; reference state: infinitely dilute solution in pyridine
X_{py}	Mole fraction of free pyridine at equilibrium
c_{py}	Molar concentration of free pyridine
γ_{py}	Rational activity coefficient of pyridine; reference state: infinitely dilute solution in chlorobenzene
γ_{cpy}	Practical activity coefficient of pyridine; reference state as above.

(19) Material supplementary to this article in the form of solubility data has been deposited as Document No. 8604 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$2.50 for photoprints or \$1.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(20) In addition, the concentration quantities relating to solutions in pure chlorobenzene are labeled with the superscript 0, whereas those relating to pyridine solutions are labeled with superscript \bullet . According to this rule, the following symbols are used: $c_4^0, c_6^0, s_4^0, s_5^0, s_6^0$.