597. *The Co-ordination Number of Transition-metal Ions. Part IV.*[1] *The Relative Stabilities of Some Tetrahedral and Octahedral Complexes of Cobalt*(II) *and Nickel*(II)

By S. M. Nelson and T. M. Shepherd

Thermodynamic data are reported for the tetrahedral–octahedral equilibria

$$ML_2I_{2(CHCl_3)} + 2L_{(CHCl_3)} \rightleftharpoons ML_4I_{2(CHCl_3)}$$

(where M = nickel(II), L = pyridine or β-picoline), and

$$ML_2I_{2(s)} + 2L_{(g)} \rightleftharpoons ML_4I_{2(s)}$$

(where M = cobalt(II) or nickel(II), L = pyridine).

The stability advantage of $Nipy_4I_2$ over $Nipy_2I_2$ (py = pyridine) is greater by ~7·2 kcal. mole^{-1} than that for the corresponding cobalt(II) case. Comparison of the experimental heat changes for these reactions with the estimated differences in crystal field stabilisation energies of the Mpy_4I_2 and Mpy_2I_2 complexes suggest that crystal field considerations alone do not adequately describe the relative stabilities of the tetrahedral and octahedral states, at least when readily polarisable ligands are involved. This conclusion is discussed in the light of the suggestion by Gill and Nyholm[2] that there is a convergence in the heats of formation of tetrahedral and octahedral complexes on passing from manganese(II) to zinc.

An interpretation of the differences in behaviour between pyridine and β-picoline complexes is suggested.

EARLIER Papers[3,4] in this Series describe the results of a thermodynamic investigation of some tetrahedral–octahedral configuration equilibria for chloroform solutions of mixed cobalt(II) complexes of the type, CoL_nX_2 (L = heterocyclic aromatic amine; X = halide or pseudohalide ion; n = 2 or 4). The work was designed to provide information about the influence of various ligand properties on the relative stabilities of the tetrahedral and

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[1] Part III, S. M. Nelson and T. M. Shepherd, preceding Paper.
[2] N. S. Gill and R. S. Nyholm, *J.*, 1959, 3997.
[3] H. C. A. King, E. Körös, and S. M. Nelson, *J.*, **1963**, 5449.
[4] H. C. A. King, E. Körös, and S. M. Nelson, *J.*, **1964**, 4832.

octahedral configurations. The results demonstrated the importance of electronic as well as steric factors in determining preferred co-ordination number, and the role of π-bonding effects was discussed. In this Paper the results of equilibrium studies of ML_nX_2 complexes both in solution and in the solid state are compared (M = Co(II) or Ni(II); L = pyridine or β-picoline; X = iodide ion).

RESULTS AND DISCUSSION

Configuration Equilibria in Solution.—Magnetic and electronic spectral properties of the solid, tetrahedral complexes $Nipy_2I_2$ and $Ni(\beta\text{-pic})_2I_2$, have been described previously by Quagliano and his co-workers;[5] we have recently reported corresponding data for octahedral $Nipy_4I_2$ and $Ni(\beta\text{-pic})_4I_2$.[1] The close correspondence between the spectra of the solid and chloroform solutions and the fact that Beer's law is obeyed indicated that the tetrahedral complexes dissolve in chloroform with little or no decomposition. In more polar solvents such as nitromethane, however, partial decomposition into ionic species was indicated by the much lower molar extinction coefficients (~140 compared with ~300 in chloroform) and the fact that these increased with increasing concentration and with added iodide ion. Molar conductivities of the nitromethane solutions ($2{\cdot}5 \times 10^{-3}$M), which were of the order of 40 mho, confirmed the presence of ionic species.

While no evidence was found for decomposition of the tetrahedral complexes in rigorously dried chloroform, spectral examination of solutions of the octahedral adducts on the other hand indicated partial dissociation into the neutral tetrahedral molecules and free amine. The dissociation could be suppressed by the addition of small amounts of free amine confirming the existence of the same type of tetrahedral–octahedral equilibrium

$$ML_2X_2 + 2L \rightleftharpoons ML_4X_2 \qquad (1)$$

described previously for cobalt(II) complexes.[3,4] No evidence for competing equilibria such as anion displacement reactions, even in chloroform–pyridine mixtures of high pyridine content was found for solutions of the nickel(II) complexes.

Equilibrium constants (K) for the association reaction (1) for the Ni–pyridine–iodide and the Ni–β-picoline–iodide systems were measured at 20° by the methods described previously.[3,4] The maximum of the ~16,900 cm.$^{-1}$ band of the tetrahedral complexes, which in T_d symmetry corresponds to the transition $^3T_1(F) \rightarrow {}^3T_1(P)$, was used for concentration measurement. Corrections for overlap by the ~16,000 cm.$^{-1}$ absorption of the octahedral complexes were made where necessary. In most cases the correction was negligible because of the very much smaller molar extinction coefficients of the octahedral complexes (~8 as compared with ~300 for NiL_2X_2). Heats of reactions were determined calorimetrically also at 20° and the associated entropy changes calculated. The results are shown in Table 1 which also includes data for the previously studied Co–pyridine–iodide system.[3]

It can be seen from a comparison of the free energy data that $Nipy_2I_2$ shows a much greater tendency to co-ordinate two further pyridine molecules than does $Copy_2I_2$. This is entirely an enthalpy effect since the entropy term is actually less favourable in the case of the nickel system. The observed preference of the nickel atom for the higher co-ordination number is in qualitative accord with the greater crystal field stabilisation energy (CFSE) in an octahedral field, and the lower CFSE in a tetrahedral field, for nickel(II) than for cobalt(II). The actual magnitude of the enthalpy difference will be discussed below in relation to crystal field effects. First of all, we shall consider the origin of the greater loss of entropy for reaction (1) for the case of M = Ni than for M = Co. In terms of the proposal outlined in Part I,[3] namely, that the high entropy loss found for the formation of $Copy_4I_2$ (relative to analogous complexes containing less polarisable anionic ligands) is due, in part, to loss of rotational freedom about the metal–amine bond as a result of a greater degree of double bonding, this would suggest an even greater measure of $d_\pi \rightarrow p_\pi$

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[5] M. D. Glonek, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1962, **84**, 2014.

overlap in the case of $Nipy_4I_2$. Indeed, this is to be expected since Ni^{2+} has an extra non-bonding 3*d* electron. A possible alternative explanation is that the difference in $-\Delta S$ (and $-\Delta H$) for the two reactions arises from differences in solvation and/or steric effects consequent upon change of the central metal ion. In view of the fact that the ionic radii of Co^{2+} and Ni^{2+} are not very different (0·72 and 0·70 Å, respectively) [6] it seems unlikely that steric effects from this source play any important part in governing rotational freedom about the metal–pyridine bond. Nor is it likely that solvation effects are very different in the two systems since the heats of solution (in chloroform) of $Copy_2I_2$ and $Nipy_2I_2$, for example, differ only by 0·4 ± 0·3 kcal. mole.$^{-1}$.

Table 1 also shows that both $-\Delta H$ and $-\Delta S$ are considerably smaller for the Ni–β-picoline–iodide system than for the corresponding pyridine system. Here solvation effects cannot be neglected since the basicities of pyridine and β-picoline ($pK_a = 5{\cdot}17$ and 5·68, respectively, at 25°) [7] are not the same and consequently different degrees of interaction (*e.g.*, hydrogen bonding) are to be expected. However, we consider it improbable that the relatively small difference in basic strength of pyridine and β-picoline could alone account for the difference of ~2 kcal. mole^{-1} in reaction (1). Support for this view is provided by the observation that the heat of solution of β-picoline in chloroform is only 0·16 kcal. mole^{-1} greater than that of pyridine in the same solvent. While it is not possible to estimate the importance of solvation effects with any precision it is worth noting that if we assume them to be small then the decreased ΔH and $-\Delta S$ for the Ni–β-picoline–iodide system are precisely the effects to be expected if β-picoline has a smaller π-acceptor capacity than pyridine. We have observed several anomalies in the behaviour of 3-alkyl-substituted pyridine complexes of cobalt(II) that are consistent with this explanation.[8] It is probably also significant that the *d*-orbital splitting is slightly less in octahedral $Ni(\beta\text{-pic})_4(NCS)_2$ than in the pyridine and γ-picoline analogues,[8] an effect not readily explained in terms of differences in the basicity of the amines.

TABLE 1

Thermodynamic data for equilibrium (1) at 20°

System	*K*	$-\Delta F$ (kcal. mole^{-1})	$-\Delta H$ (kcal. mole^{-1})	$-\Delta S$ (cal. deg.$^{-1}$ mole^{-1})
$Nipy_2I_2$	31,000	6·02 ± 0·04	23·8 ± 0·4	60·7 ± 1·5
$Ni(\beta\text{-pic})_2I_2$	9500	5·34 ± 0·04	21·7 ± 0·4	55·8 ± 1·5
$Copy_2I_2$	2·32	0·49 ± 0·03	16·6 ± 0·2	54·9 ± 1·0

Configuration Equilibria in the Solid State.—A method of preparation of both $Copy_2I_2$ and $Nipy_2I_2$ is to remove two molecules of pyridine from the corresponding octahedral adducts by heating. The cobalt complex can be obtained in this way even at temperatures little above ambient while for $Nipy_2I_2$ temperatures above ~80° are best employed. The marked difference in the ease of removal of pyridine in the two cases was considered to be a reflection of stronger binding in the nickel system. In order to confirm this and to compare with the analogous solution equilibria the equilibrium dissociation vapour pressures of pyridine for the two systems were measured as a function of temperature. Both equilibria appeared to be completely reversible as the same equilibrium pressure for a given temperature could be obtained either by approach from a higher or a lower temperature. Equilibrium was usually established in under two hours; in general, equilibrium times were considerably shorter at the higher temperatures. In each case the temperature variation of the dissociation pressure (see Table 2) can be expressed in the form

$$\log_{10} p \text{ (mm. Hg)} = A - (B/T)$$

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[6] L. Pauling, " The Nature of the Chemical Bond," Cornell University Press, New York, 1948.

[7] H. C. Brown, D. H. McDaniel, and O. Hafliger, " Dissociation Constants," in E. A. Braude and F. C. Nachod, " Determination of Organic Structures by Physical Methods, Academic Press Ind., New York, 1955.

[8] H. C. A. King, S. M. Nelson, and T. M. Shepherd, unpublished results.

TABLE 2

Dissociation vapour pressure of pyridine as a function of temperature for reaction (2)

M = Co		M = Co		M = Ni	
T(°K)	p (mm. Hg)	T(°K)	p (mm. Hg)	T(°K)	p (mm.H g)
302·3	0·60	322·4	4·00	358·7	0·92
306·1	0·76	328·7	6·95	365·0	1·52
309·5	1·23	334·5	11·20	371·2	2·51
313·6	1·80	339·3	16·24	376·4	3·83
317·7	2·65	340·6	18·02	382·9	6·25
				387·8	9·07
				393·0	12·90

The average values of the constants A and B are summarised in Table 3, which also includes values of ΔF^0_{293}, ΔH^0_{293}, and ΔS^0_{293} for the reactions expressed as

$$\mathrm{Mpy_2I_{2(s)}} + \mathrm{2py_{(g)}} \rightleftharpoons \mathrm{Mpy_4I_{2(s)}} \qquad (2)$$

The thermodynamic functions were calculated on the assumption that the heat changes are constant over the temperature range and that pyridine behaves as an ideal gas.

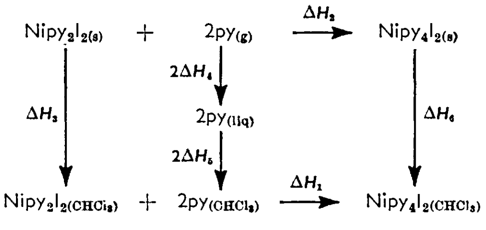
TABLE 3

Thermodynamic data for equilibrium (2) at 20°

System	A	B	$-\Delta F°_{293}$ (kcal. mole^{-1})	$-\Delta H°_{293}$ (kcal. mole^{-1})	$-\Delta S°_{293}$ (cal. deg.$^{-1}$ mole^{-1})
$Nipy_2I_2$	13·18	4745	15·81 ± 0·05	43·44 ± 0·3	94·2 ± 1·3
$Copy_2I_2$	12·93	3976	9·44 ± 0·05	36·20 ± 0·3	92·0 ± 1·3

The enthalpy changes for reaction (2) are, of course, not directly comparable with those for reaction (1) since they include terms for the heats of solution of the solid complexes in chloroform and for heat of condensation and heat of solution of pyridine. However, the differences in the enthalpy changes for the two solid configuration equilibria, ΔH_2(Ni) — ΔH_2(Co), should be comparable with the corresponding enthalpy difference for the solution equilibria, ΔH_1(Ni) — ΔH_1(Co). This is because it is unlikely that replacement of the central cobalt atom by the slightly smaller nickel atom leads to any serious change in the molecular lattice energies of either the tetrahedral or octahedral complexes. That this is so for the two tetrahedral complexes is demonstrated by their similar heats of solution in chloroform. In accord with this we find that ΔH_1(Ni) — ΔH_1(Co) and ΔH_2(Ni) — ΔH_2(Co) are in remarkably close agreement, —7·20 and —7·24 kcal. mole^{-1}, respectively.

As a further check on the experimental data the observed ΔH_2 for the nickel system may be compared with the value calculated by means of the thermochemical cycle.



From Hess' law

$$\Delta H_2 = \Delta H_1 + \Delta H_3 + 2\Delta H_4 + 2\Delta H_5 - \Delta H_6$$

where ΔH_3 = heat of solution of $Nipy_2I_2$ in chloroform, ΔH_4 = heat of condensation of pyridine, ΔH_5 = heat of solution of pyridine in chloroform, ΔH_6 = heat of solution of $Nipy_4I_2$ in chloroform (containing ~3% added pyridine to suppress dissociation). The literature value [9] of ΔH_4 = —9·68 kcal. mole^{-1} was used; ΔH_1 is given in Table 1; ΔH_3,

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[9] J. D. Cox, A. R. Challoner, and A. R. Meetham, *J.*, 1954, 265.

ΔH_5, and ΔH_6 were found by experiment to be 1·40 ± 0·15, −2·44 ± 0·05, and −2·40 ± 0·15 kcal. mole^{-1}, respectively. ΔH_2 is thus calculated as −44·24 ± 0·82 kcal. mole^{-1}, which, within the combined experimental errors, is the same as the experimental value of −43·44 ± 0·3 kcal. mole^{-1}.

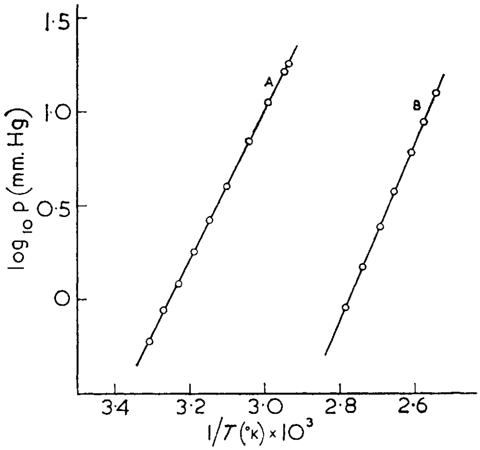
Crystal Field Stabilisation Energies.—It is of interest to compare the experimental $\Delta H(\text{Ni}) - \Delta H(\text{Co})$ value (−7·2 kcal. mole^{-1}) with the CFSE difference

$$\{\text{CFSE}(\text{Ni}_{\text{oct}}) - \text{CFSE}(\text{Ni}_{\text{tet}})\} - \{\text{CFSE}(\text{Co}_{\text{oct}}) - \text{CFSE}(\text{Co}_{\text{tet}})\},$$

which may be written as

$$\{6/5\Delta(\text{Ni}_{\text{oct}}) - 4/5\Delta(\text{Ni}_{\text{tet}})\} - \{4/5\Delta(\text{Co}_{\text{oct}}) - 6/5\Delta(\text{Co}_{\text{tet}})\} \qquad (3)$$

where Δ is the crystal field splitting parameter. There is difficulty in evaluating these parameters for the complexes considered here. The electronic spectra of all four complexes indicate deviations from regular symmetry as a result, presumably, of the widely separated positions of pyridine and iodide in the spectrochemical series.[1,3,5] Thus, in the 6-co-ordinate complexes there appears to be considerable tetragonal distortion while in the 4-co-ordinate complexes there is a C_{2v} component to the field. However, by comparing the spectra with those of related complexes [10] and assuming the rule of average environment to be approximated it is possible to make reasonable estimates of the *d*-orbital splitting that would occur in the absence of distortion. Accordingly, we have taken Δ to be 9200 cm.$^{-1}$ for both Nipy_4I_2 and Copy_4I_2, 5000 cm.$^{-1}$ for Nipy_2I_2 and 3800 cm.$^{-1}$ for Copy_2I_2. By substituting these values into expression (3) a value of −12·1 kcal. mole^{-1} is obtained. While considerable uncertainty must exist in view of the approximations and assumptions involved, this value is unlikely to be in error by more than 1 to 2 kcal. mole^{-1}, and, is in any case, substantially larger than the experimentally determined value (−7·2 kcal. mole^{-1}) of $\Delta H(\text{Ni}) - \Delta H(\text{Co})$.



Dissociation vapour pressure of pyridine as a function of temperature for reaction (2)
Curve A, M = Co; Curve B, M = Ni

The implication of this discrepancy is that the stability difference between Nipy_2I_2 and Nipy_4I_2, when corrected for CFSE, is less by about 5 kcal. mole^{-1} than the corresponding stability separation between Copy_2I_2 and Copy_4I_2, *i.e.*, there is a convergence in the CFSE corrected heats of formation of the tetrahedral and octahedral complexes. This suggestion was made previously by Gill and Nyholm [2] from qualitative estimates of the relative stabilities of $[\text{MHal}_4]^{2-}$ ions in various solvents (M = bivalent metal ions, Mn to Zn).

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[10] C. K. Jørgenson, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962; " Inorganic Complexes," Academic Press, London, 1963, and references contained therein; D. M. L. Goodgame and M. Goodgame, *J.*, 1963, 207; F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690, and subsequent Papers by same authors.

Blake and Cotton[11] recently observed a similar effect in their investigation of the thermodynamics of the reaction $[MCl_4]^{2-}{}_{(aq)} + aq. = [M(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)}$. It should be pointed out, however, that although the latter authors found the closing of the gap to be considerable (5·5—7·0 kcal. mole^{-1}) on passing from Co(II) to Ni(II), the mean overall effect on passing from Mn(II) to Zn was much smaller, only ~1 kcal. mole^{-1} per element. They point out that the metal–ligand bond energy should not be assumed to be a smoothly varying function of atomic number even in a series of homologous complexes. It would therefore be unwise to extrapolate our results on the relative stabilities of tetrahedral and octahedral Co(II) and Ni(II) complexes to Mn(II) and Zn for which CFSE = 0. However, there is independent evidence for a convergence of the kind mentioned. A survey of the literature reveals that while octahedral complexes of Mn(II) are very common, few tetrahedral complexes are known. Examples are the tetrahalogenomanganese(II) anions[12] and certain mixed complexes of the type MnL_2Hal_2 (L = phosphine oxide or arsine oxide).[13] The only Mn(II)–pyridine complexes which, to our knowledge, have been structurally characterised are $Mnpy_2Cl_2$ and $Mnpy_2Br_2$, both of which have octahedral configurations.[14] On the other hand there is abundant information that zinc prefers co-ordination number 4 rather than 6, at least when the co-ordinating atoms are nitrogen or halogen. For example, $Znpy_2Cl_2$, $Znpy_2I_2$, and $Zn(NH_3)_2Cl_2$ are all tetrahedral.[15] We have also examined a number of other ZnL_2X_2 complexes of this type (L = heterocyclic amine) by *X*-ray and infrared methods and in no case have we found structures other than tetrahedral.[16] Finally, Uruska and Libus[17] have recently found, from solubility studies in chlorobenzene–pyridine mixtures, that $Znpy_2Cl_2$ shows no affinity for the co-ordination of two further pyridines, in contrast to the results for Co(II) and Ni(II) complexes. In general agreement with this we have been unable to prepare in the solid state any stable mononuclear octahedral complexes of the type ZnL_4X_2.

It may be concluded, therefore, that there is considerable evidence in favour of an increasing stability of the tetrahedral state, relative to the octahedral, on passing from Mn(II) to Zn. As Gill and Nyholm have suggested this is probably due to increased covalence in the metal–ligand bonds of the tetrahedral complex as the electron affinity of the central metal ion increases.[2] It is to be expected that the effect should be most marked in complexes containing readily polarisable ligands, *e.g.*, iodide ion, such as are described above.

EXPERIMENTAL

The preparation of the complexes has been described previously,[1,3,5] as have also the methods employed in the measurement of association constants and heats of reaction in chloroform solution.[3,4] The chloroform (AnalaR quality) was double distilled before use and dried for several days over a molecular sieve. Pyridine (AnalaR) and β-picoline (B.D.H.) were similarly treated. Rigorous drying of materials was found to be essential for all work involving the tetrahedral nickel(II) complexes since these are very hygroscopic. Slight deviations from Beer's law were observed for solutions of these complexes in imperfectly dried solvent.

Dissociation pressures were measured in a glass isotenoscope in which mercury was used as confining liquid and as a tap to the vacuum train. After the glass bulb containing the powdered sample was sealed into the system, the entire bulb and manometer assembly was immersed in an oil-bath capable of temperature control to ±0·1°. The sample was degassed for several hours at room temperature in the case of $Copy_4I_2$, and for one day at 50° in the case of $Nipy_4I_2$.

[11] A. B. Blake and F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 5.

[12] S. Buffagni and T. M. Dunn, *Nature*, 1960, **188**, 937; F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1962, **84**, 167.

[13] D. M. L. Goodgame and F. A. Cotton, *J.*, 1961, 3735.

[14] R. W. Asmussen, Symposium on Co-ordination Chemistry, Copenhagen, 1953, p. 27.

[15] N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nuclear Chem.*, 1961, **18**, 88; C. H. MacGillavry and J. M. Bijoet, *Z. Krist.*, 1936, **94**, 231.

[16] S. M. Nelson and T. M. Shepherd, unpublished results.

[17] I. Ursuska and W. Libus, Proceedings of 8th International Conference on Co-ordination Chemistry, Vienna, 1964, p. 340.

Mercury manometer levels were followed by observation through a travelling microscope. Several measurements of the equilibrium pressure were taken at each temperature, the pyridine vapour being pumped out between each, in order to ensure complete removal of air. Measurements were taken at approximately 5° intervals in the range 30—70°, for $\mathrm{Copy_4I_2}$, and in the range 85—120° for $\mathrm{Nipy_4I_2}$. Corrections for the temperature variation of the density and vapour pressure of mercury were made. The equilibrium constants and calorimetric heats of reaction in solution were measured as described previously.[3,4]

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