been observed for nonchelated amino acid complexes.[14] Shimura[16] used the term *vicinal effect* for the optical activity observed for [Co(NH₃)₄-(S)-leu](ClO₄)₂. Although the term vicinal effect implies that the optical activity arises from the presence of the asymmetric center in the ligand, it has not been used in such a limited sense, but to include all contributions other than that from the spiral arrangement of the chelate rings.

The appearance of two CD peaks for the resolved complexes in the first ligand field band region would be consistent with effective D_3 symmetry. The effective symmetry must be lower, however, since, in the second band region, E (T_{2g}) is allowed, but A_1 (T_{2g}) is not for D_3 symmetry.[17] Two CD peaks are observed in this region except for (+)-D-[Co(en)₂-(S)-met]I₂, for which three weak peaks are apparent (Figure 1). The CD spectrum was checked on a Jasco instrument. Three CD peaks in this region have been observed also for some of the corresponding complexes of other amino acids.[8] Three CD peaks in the T_{2g} region, three peaks in the first-band region for [Co(NH₃)₄-(S)-palan]I₂[8] and similar complexes,[14] and three peaks in the first-band region for the unresolved complex strongly suggest that the effective symmetry is low enough and the splitting is great enough for the complete removal of

(16) Y. Shimura, *Bull. Chem. Soc. Japan*, **31**, 315 (1958).
(17) S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

degeneracy. Except in these favorable cases, some peaks are masked by more intense neighboring peaks of opposite sign. It does not appear reasonable to expect that three apparent peaks result from the overlap of two peaks of greatly different band widths. Since the same effective symmetry must pertain to Δ- or Λ-[Co(en)₂-(S)-aa]I₂, the same splittings would result. The differences among the resulting CD curves should arise from varying intensity contributions for each of the transitions from the sources cited for an optically active ligand and from the chiral pattern of the chelate rings in the resolved isomers. The CD spectrum is dominated by the contributions from the ring chirality for the resolved complexes. Apparently the conformational contributions for en rings is negligible in these cases.

The dengeneracy of the T levels is removed in C_{2v}, C_2, or C_1 symmetry. The molecular symmetry is C_1 for these complexes, but assignments have no significance for C_1 symmetry since the only representation is A. The X-ray determination of the absolute configuration[6] makes it clear that the sign of the dominant CD peak in the first-band region is derived from E_a (D_3) parentage.

Thermodynamic Studies of the Relative Stabilities of Bis- and Tris-Phosphine Complexes of Nickel(II) Cyanide in Solution

BY P. RIGO, G. GUASTALLA, AND A. TURCO

Thermodynamic data are reported for the four-coordinate–five-coordinate equilibria Ni(PR₃)₂(CN)₂ + PR₃ ⇌ Ni(PR₃)₃-(CN)₂ (where PR₃ = P(C₂H₅)₃, P(C₃H₇)₃, P(C₄H₉)₃, P(C₂H₅)₂C₆H₅, PC₂H₅(C₆H₅)₂) in ethanol, *n*-hexane, and dichloroethane. The stability order for the complexes Ni(PR₃)₃(CN)₂, measured by the equilibrium constants at 20° in ethanol, is P(C₃H₇)₃ ~ P(C₄H₉)₃ < P(C₂H₅)₃ < PC₂H₅(C₆H₅)₂ ≪ P(C₂H₅)₂C₆H₅. It is shown that the values of the enthalpy changes $\Delta H°$, determined spectrophotometrically by measuring the equilibrium constants at different temperatures, provide a fairly good measure of the growing covalency of the bonds on formation of the five-coordinate complexes.

Complexes with various coordination numbers are formed by nickel(II) and cobalt(II) in their compounds with trisubstituted phosphines and anionic ligands. When the anionic partners X are weak-field ligands, tertiary phosphines give only the four-coordinate complexes M(P)₂X₂[1,2] (where P is the phosphorus atom of a tertiary phosphine). With ditertiary phosphines, in addition, the cationic five-coordinate com-

pounds M(P)₄X⁺ can be obtained in which four phosphorus atoms are bound to the metal ion. The possibility to give the neutral five-coordinate complexes M(P)₃X₂ with both tertiary and ditertiary phosphines appears to be restricted to compounds containing "strong" anions such as CN⁻ or also NCS⁻ in the case of cobalt(II).[3,4] As a part of the investigations carried on in order to elucidate the factors which

(1) T. Boschi, M. Nicolini, and A. Turco, *Coord. Chem. Rev.*, **1**, 269 (1966).
(2) P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).

(3) P. Rigo, M. Bressan, and A. Turco, *ibid.*, **7**, 1460 (1968).
(4) P. Rigo, B. Corain, and A. Turco, *ibid.*, **7**, 1623 (1968).

Table I

Stability Constants (K, M^{-1}) for the Equilibrium $Ni(PR_3)_2(CN)_2 + PR_3 \rightleftarrows Ni(PR_3)_3(CN)_2$

PR3	Solvent	Temp, °C							
		−30	−20	−10	0	10	20	30	40
P(C2H5)3	C2H5OH	...	...	...	53.3 ± 2.4	25.2 ± 1.0	13.4 ± 0.4	7.5 ± 0.15	...
	C2H4Cl2	...	...	...	10.3 ± 0.1	4.1 ± 0.2	1.9 ± 0.03	...	...
P(C2H5)2C6H5	C2H5OH	...	...	...	...	3260 ± 145	1320 ± 82	490 ± 26	...
	C2H4Cl2	...	...	...	...	...	93.3 ± 3.6	34.2 ± 1.7	12.6 ± 0.2
P(C6H5)2C2H5	C2H5OH	...	...	...	...	52.0 ± 0.5	32.2 ± 1.1	23.4 ± 0.6	...
	C2H4Cl2	...	...	...	...	4.1 ± 0.2	2.4 ± 0.08	1.4 ± 0.02	...
P(C3H7)3	C2H5OH	...	43.0 ± 2.0	18.6 ± 0.6	8.20 ± 0.25	3.4 ± 0.15	...	...	...
	n-Hexane	60.3 ± 1.4	24.6 ± 1.1	9.9 ± 0.4	4.4 ± 0.2	...	...	...	...
P(C4H9)3	C2H5OH	...	...	26.6 ± 0.7	12.4 ± 0.4	5.6 ± 0.3	2.8 ± 0.1	...	...
	n-Hexane	57.2 ± 0.01	22.5 ± 0.6	10.9 ± 0.4	4.8 ± 0.1	...	...	...	...

determine the stability of these neutral "tris-phosphine" complexes, in a previous paper we reported the results of a thermodynamic investigation of the equilibrium

$$Co(PR_3)_2(NCS)_2 + PR_3 \rightleftarrows Co(PR_3)_3(NCS)_2 \quad (1)$$
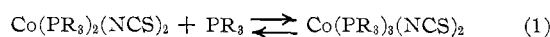
where R = alkyl or aryl.[5] The chief aim of that work was to study the energetics of the addition reaction which, starting from high-spin tetrahedral complexes, leads to the formation of low-spin five-coordinate complexes. In the present paper we report the results of equilibrium studies on the reaction

$$Ni(PR_3)_2(CN)_2 + PR_3 \rightleftarrows Ni(PR_3)_3(CN)_2 \quad (2)$$
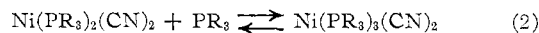
in which the reactant species are all diamagnetic.[2]

In contrast to the substantial amount of thermodynamic data published on equilibria of ionic complexes in water, very little work has been done on equilibria involving neutral complexes reacting with neutral ligands in nonaqueous weakly coordinating solvents. Most of the work published deals with the formation of six-coordinate complexes of cobalt(II) or nickel(II) from four-coordinate[6] and five-coordinate complexes.[7]

Experimental Section

Electronic spectra were recorded with an Optica CF4NI double-beam spectrophotometer. Molar conductivities were determined at 25°. The absence of quaternization processes of the phosphines in C2H4Cl2 was ascertained by the negligible changes in conductivity during the time necessary to carry out the spectrophotometric measurements (10 min).

The complexes of nickel(II) were prepared according to published methods by heterogeneous reaction of the phosphine with Ni(CN)2.[2,4] The phosphines were prepared by Grignard methods and were distilled twice *in vacuo* before use.

Solvents were purified and dried by standard methods and distilled twice under a nitrogen atmosphere just prior to use.

Measurement of Equilibrium Constants.—These were carried out spectrophotometrically by a method similar to that described by Hammond.[8] The optical densities were measured at the maximum of the band typical of the five-coordinate complexes (410–440 mμ).[2] The absorption of the planar compounds is negligible in this region of the spectrum.

An isosbestic point was observed for all of the solutions in the region of 340–370 mμ, indicating the presence of two absorbing species only. Inspection of the spectra even in the presence of

large excess of phosphine ruled out the possibility that species with coordination numbers different from 4 and 5 could be formed. The formation of ionic species was ruled out by measuring the conductivities of the solutions in C2H5OH and C2H4Cl2.

To obtain K, various solutions of the complex, of the same known concentration ($\sim 10^{-3}$ M), were prepared containing different known amounts of phosphine. K was calculated by the equation $x/A = (1/K\epsilon c) + (x/\epsilon c)$, where x is the molar concentration of the added phosphine ($x > 10c$), A is the optical density for the 1-cm light path, ϵ is the molar absorbance, and c is the constant concentration of the complex. The values of K and ϵ can be estimated from the intercept and slope of the graphs of x/A vs. x.

The plots of x/A vs. x gave straight lines. K and ϵ were calculated from the values of the intercepts and of the slopes estimated by the least-squares method. The single values of K were determined with a minimum of six runs in which the concentration of the phosphine was changed by at least a factor of 5. The values of x used were in the range 5×10^{-3}–5×10^{-1} depending upon the value of the stability constant.[9] The ranges of concentrations were selected in such a way that the percentage of the four-coordinate complex was maintained within the limits of 20–80%. The standard error in K was calculated from the standard errors in the $1/\epsilon c$ and $1/K\epsilon c$ values, evaluated by the least-squares method. The relative error (standard error divided by the value of K) calculated for the values of K was in the range 1–5%. The complex $Ni(P(C_2H_5)_2C_6H_5)_3(CN)_2$ is too stable in ethanol to permit the estimation of the stability constant in excess phosphine as required by the previous method. In this case the equilibrium was studied with the method described by Denning, *et al.*[10] The apparent extinction coefficients ϵ_1 (8000–9000) at the single temperatures were measured directly in excess of phosphine. Approximate values of K were calculated using ϵ values in the range of $\epsilon_1 \pm 300$. Finally the best value of the equilibrium constant was calculated using the value of ϵ which minimizes the standard deviation of K. The equilibrium constants are reported in Table I.

The $\Delta H°$ values were obtained from plots of log K vs. $1/T$ by measuring the equilibrium constants at three or four different temperatures at intervals of 10°. The temperatures were selected in the range of −30 to +40°. Errors in $\Delta H°$ and $\Delta S°$ were calculated following the procedure suggested by Denning, *et al.*,[10] and are reported in Table II.

The temperature coefficient method was chosen over the calorimetric method because it gave more reliable results in the systems studied. Calorimetric measurements were found to be affected by several potential sources of error.

The first important complication arose from the occasional

(5) T. Boschi, P. Rigo, C. Pecile, and A. Turco, *Gazz. Chim. Ital.*, **97**, 1391 (1967).

(6) S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 3284 (1965).

(7) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

(8) P. B. Hammond, *J. Chem. Soc.*, 479 (1964).

(9) The data have been deposited as Document No. NAPS-00145 with the ASIS National Auxiliary Publication Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $3.00 for photocopies or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(10) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 324 (1967).

TABLE II

THERMODYNAMIC DATA FOR THE EQUILIBRIUM $Ni(PR_3)_2(CN)_2 + PR_3 \rightleftharpoons Ni(PR_3)_3(CN)_2$ at 20°

PR₃	—ΔH°, kcal/mol—			—ΔS°, eu—		
	C₂H₄Cl₂	C₂H₅OH	n-Hexane	C₂H₄Cl₂	C₂H₅OH	n-Hexane
$P(C_2H_5)_3$	13.4 ± 0.2	10.7 ± 0.4	...	44 ± 1	31 ± 1	...
$P(C_2H_5)_2C_6H_5$	18.6 ± 0.5	16.1 ± 0.8[a]	...	54 ± 2	41 ± 3	...
$PC_2H_5(C_6H_5)_2$	8.9 ± 0.5	6.8 ± 0.3	...	29 ± 2	16 ± 1	...
$P(C_3H_7)_3$	...	12.0 ± 0.4	11.6 ± 0.3	...	40 ± 2	39 ± 1
$P(C_4H_9)_3$	...	11.6 ± 0.4	10.8 ± 0.4	...	38 ± 1	36 ± 1

[a] Calorimetric determination, 17.0 kcal.

presence of traces of oxygen, which reacts exothermically with the phosphines. Further, the stability of the five-coordinate complexes was generally too low to allow the reaction to go to completion for reasonable values of the concentrations. Moreover small values of K were accompanied by small values of $\Delta H°$ (Table III), thus making the measured heats of reaction very small. For all of these reasons the calorimetric method was used

TABLE III

INTEGRAL HEATS OF SOLUTION OF $Ni(PR_3)_2(CN)_2$ COMPLEXES
(KCAL/MOL)

PR₃	C₂H₄Cl₂	C₂H₅OH	n-Hexane
$P(C_4H_9)_3$	+4.7	+6.6	+7.9
$P(C_2H_5)_3$	...	+5.8	...

only as a check of a $\Delta H°$ value obtained with the temperature coefficient method. The equilibrium reaction with $P(C_2H_5)_2C_6H_5$ was selected because it appeared to be the most favorable case, considering the relatively large values of K and $\Delta H°$.

Calorimetric Measurements.—A calorimeter equipped with a thermistor for the detection of temperature changes was used. The calorimeter was immersed in a water thermostat bath at 20 ± 0.1°. Calibrations for each run were carried out electrically.

The over-all accuracy of the calorimeter was tested by measuring the integral heat of solution of solid potassium chloride in water at 25°. The mean value found for ΔH was 4199 ±6 cal/mol for a molar ratio 1:200, in good agreement with other values in the literature (4199,[11] 4191[12]).

The enthalpy of the reaction of $Ni(P(C_2H_5)_2C_6H_5)_2(CN)_2$ with $P(C_2H_5)_2C_6H_5$ (Table II) was measured in a nitrogen atmosphere. A thin glass bulb containing a weighed amount of phosphine (about 1.5 g) was broken in a solution containing a known amount of the complex (about 0.4 g) in 150 g of ethanol, and the apparent heat of reaction was measured. The integral heat of solution of the phosphine was measured in other experiments dissolving weighed amounts of phosphine (about 1.5 g) in 150 g of ethanol. The measured heat of solution was 9.99 ± 0.24 kcal/mol. The enthalpy of the reaction was determined from the apparent heat of reaction and the integral heat of solution of the phosphine.

The integral heats of solution of the complexes $Ni(PR_3)_2(CN)_2$ were measured at a constant complex:solvent molar ratio of 1:1430. ΔH values listed in Table III are averages of several determinations in each case. The estimated experimental error in the ΔH values was ±0.5%.

Results and Discussion

The thermodynamic functions for equilibrium 2 are summarized in Table II. It should be noted that the data have been obtained in different solvents and

(11) P. Paoletti, R. Usenza, and A. Vacca, *Ric. Sci. Rend., Sez. A*, **8**, 201 (1965).

(12) G. Somsen, J. Coops, and M. W. Tolk, *Rec. Trav. Chim.*, **82**, 231 (1963).

therefore in the comparison a correction must be made for the cratic term. This correction is however very small and can be neglected within the limits of precision of the data required in the present discussion.

Table II shows that the values of $\Delta H°$ and $\Delta S°$ are all negative and notably large in some cases. This is not surprising since the equilibria involve neutral species in relatively weakly coordinating solvents. In these reactions the solvent molecules play a minor role and the gain of desolvation heats or entropies cannot compensate for the corresponding loss resulting from the coordination reactions.

The data for equilibrium 2 in n-hexane are of particular interest, because solvation is certainly of very limited importance in this solvent. The comparison with the data in ethanol shows that solvation does not play a large role in the latter solvent, as shown by the fact that $\Delta H°$ is practically identical in ethanol and n-hexane. Thus, if we assume that solvation heats in n-hexane are of negligible importance, from the almost identical results in ethanol we can conclude that the values of $\Delta H°$ in the latter solvent are a good measure of the *over-all increase of covalency in going from the planar to the five-coordinated complexes*.[18] Regardless of the electronic mechanism of stabilization (CN^- and PR_3 can both be considered to form good σ and π bonds), one can say that it is the large loss of heat which provides the driving force for the formation of the five-coordinated adducts, counteracting the generally large decrease of entropy.

The data in Table II show that there is a strict correlation between the entropy and enthalpy change. Larger values of $-\Delta H°$ invariably involve larger $-\Delta S°$ values. This is particularly evident in the series $P(C_2H_5)_3$, $P(C_2H_5)_2C_6H_5$, and $PC_2H_5(C_6H_5)_2$, but is also true for all of the cases listed in Table II, as shown by the data in ethanol. The increments in the values of $\Delta H°$ and $\Delta S°$ are constant, within the limits of the estimated errors, in the different solvents on changing the phosphines. For example on going from $P(C_2H_5)_3$ to $P(C_2H_5)_2C_6H_5$ $\Delta(\Delta H°)$ is 5.2 in $C_2H_4Cl_2$ and 5.4 in ethanol; $\Delta(\Delta S°)$ is 10 in both solvents. The changes on going from $P(C_2H_5)_2C_6H_5$ to $PC_2H_5(C_6H_5)_2$ in the two solvents are: $\Delta(\Delta H°) = 9.7$, 9.3; $\Delta(\Delta S°) = 25$, 25. This behavior demonstrates very clearly that the changes of $\Delta H°$ and $\Delta S°$ on varying the nature of the phosphine in a single solvent

(13) S. Ahrland, *Helv. Chim. Acta*, **50**, 306 (1967).

are entirely associated with the coordination process and are not due to different solvation effects. Therefore, if the value of $\Delta H°$ is a measure of the change in the over-all bond energy, the observed correlation between $\Delta H°$ and $\Delta S°$ means that as the five-coordinate compound becomes more covalent (relative to the four-coordinate), its rigidity increases. It seems reasonable to attribute this correlation between $\Delta H°$ and $\Delta S°$ to the greater importance of restricted rotation of the ligands as the bonds become more covalent. This, however, may be due to increased importance of π bonding. Without attempting further speculative explanations in terms of σ or π bonding, we wish to emphasize the drastic changes in bonding properties, reflected by the changes of $\Delta H°$, which occur in the series $P(C_2H_5)_3$, $P(C_2H_5)_2C_6H_5$, and $PC_2H_5(C_6H_5)_2$. The variation in the thermodynamic parameters is particularly important on going from $P(C_2H_5)_2C_6H_5$ to $PC_2H_5(C_6H_5)_2$ and it is pertinent here to remember that, for some of the four-coordinate complexes Ni-$(PR_3)_2X_2$, in the series $P(C_2H_5)_3$ to $P(C_6H_5)_3$ the transition from diamagnetic to paramagnetic compounds is found with $PC_2H_5(C_6H_5)_2$.[14]

The effect of the solvent on the thermodynamic parameters merits a brief comment. For experimental reasons it has not been possible to study all of the equilibria in the solvents of Table II. Nevertheless a comparison is still possible. Within the limits of the probable error, the values of $\Delta H°$ and $\Delta S°$ are, respectively, identical for the complexes with $P(C_3H_7)_3$ and $P(C_4H_9)_3$ in ethanol and n-hexane. This result is rather surprising because ethanol is expected to solvate the reacting species more than n-hexane. Precise knowledge about the effects of neutral solutes on the structure of liquid alcohols is lacking. The association of alcohols in hydrogen-bonded chains is a well-established fact;[15] however, it is not easy to decide *a priori* if the solute molecules will be structure breaking or structure forming. The data in Table II mean that the enthalpy and entropy changes involved by solvation in ethanol are balanced in such a way that the final net changes of $\Delta H°$ and $\Delta S°$ in equilibrium 2 are the same as in n-hexane. To check the validity of these arguments, the integral heats of solution of the complex $Ni(P(C_4H_9)_3)_2(CN)_2$ were measured calorimetrically in $C_2H_4Cl_2$, ethanol, and n-hexane (Table III). The difference of the heats of solution, determined at practically infinite dilution, is a measure of the difference of heats of solvation, that is of the heats involved by the rearrangement of the solvent molecules in the solvation process. The data in Table III show that the difference between ethanol and n-hexane is very small (1.3 kcal/mol) indicating that heats of solvation play a role of comparable importance in the two solvents.

The solvation process in $C_2H_4Cl_2$ is slightly more exothermic than in ethanol. This result is not surprising in view of the previous discussion and considering that the solvating power of $C_2H_4Cl_2$ is certainly higher than that of n-hexane. It is pertinent here to remember that CH_2Cl_2, a similar compound, shows a definite coordinating power, being retained with constant stoichiometry on crystallization of some planar complexes.[16] In this respect, we cannot offer a simple explanation for the fact that $\Delta H°$ and particularly $\Delta S°$ of equilibrium 2 are larger in $C_2H_4Cl_2$ than in ethanol. A preferential solvation of the five-coordinate adducts by $C_2H_4Cl_2$, combined with the effects arising from the association of ethanol, might justify this result.

(14) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **4**, 1701 (1965), and references therein.

(15) F. Franks and D. J. G. Ives, *Quart. Rev.* (London), **20**, 1 (1966).

(16) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1347 (1967).