

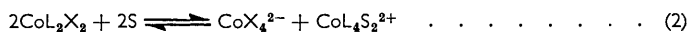
without apparent reason. For example, $\text{Co}(\text{3-methylpyridine})_2(\text{NCS})_2$ has a tetrahedral configuration whereas the 4-methylpyridine analogue is octahedral.⁶ It may be that, in addition to the fairly obvious intramolecular steric effects which occur in some cases (as in the 2-methylpyridine complexes to be described in this paper), crystal packing can be a deciding factor. In any event, a delicate balance of several effects is probable and a small change in the contribution of any one may cause stereochemical rearrangement. To evaluate the roles of the charge distribution in the metal-ligand bond and of intramolecular steric effects in situations not affected by lattice forces we have examined quantitatively the degree of co-ordinative unsaturation of the metal atom in the tetrahedral state by a study of the position of equilibrium of the following configurational change in solution



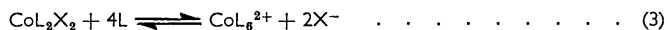
where L = pyridine or 2-methylpyridine and X = Cl^- , Br^- , I^- , OCN^- , SCN^- , or SeCN^- . Chloroform was chosen as solvent because it is the least polar solvent which will dissolve all the complexes. Even in chloroform some were difficultly soluble and a selected number of measurements were therefore made with nitromethane solutions. Spectrophotometric determination of equilibrium constants, by the method of Sacconi *et al.*,⁷ was possible because of the separate well-defined visible spectra of the two configurational species. Enthalpies of reaction were determined calorimetrically, where possible, and the corresponding entropy terms were calculated.

RESULTS AND DISCUSSION

Before considering the thermodynamic results it is necessary to establish that the only equilibrium occurring in the solutions investigated is that represented in (1). Other possibilities are the reactions



where S = solvent; and, in the presence of an excess of ligand,



Reaction (2), in dimethylformamide solutions of $\text{Co}(p\text{-toluidine})_2(\text{NCS})_2$, was found by Cotton and Holm;⁸ the second type of ligand exchange occurs in strongly dissociating solvents such as water. However, decomposition in the solutions for which we have thermodynamic data can be eliminated on the basis of several lines of reasoning:

(1) The 580—680 $\text{m}\mu$ absorption of the complexes in chloroform solution (see Table I) obeyed Beer's law, and the spectral bands were distinct, in position and profile, from the known spectra^{2b,9} of the corresponding CoX_4^{2-} species (compare curves C and D, Fig. 1). Further, in none of the solutions was there evidence of weak absorption in the region of 480—550 $\text{m}\mu$ which might be expected for solvated ions of the type $\text{CoL}_x\text{S}_{6-x}^{2+}$

(2) On addition of pyridine the 580—680 $\text{m}\mu$ absorption remained unchanged in position, falling only in intensity and finally disappearing as the pyridine content was further increased. The bands which then appeared at 480—550 $\text{m}\mu$ (Table I) and increased in intensity with increase in the amount of pyridine added were different for each complex, the differences being in accord with expectations based on the position of X in the spectrochemical series; none of the spectra corresponded to that of the ion Co py_6^{2+} (curve A, Fig. 1). An isosbestic point was observed for these solutions, as the concentration of pyridine was varied (see Fig. 2), indicating the presence of two absorbing species only.

Fig. 2 requires some comment. Two absorption maxima are shown, one at 525 $\text{m}\mu$

⁶ Nelson, unpublished work.

⁷ Sacconi, Lombardo, and Paoletti, *J.*, 1958, 848.

⁸ Cotton and Holm, *J. Amer. Chem. Soc.*, 1960, **82**, 2983.

⁹ Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 1777; Turco, Pecile, and Niccolini, *Proc. Chem. Soc.*, 1961, 213.

TABLE I.

Complex	State	Conductance of 10 ⁻³ M solutions (mho) at 20°	$\lambda_{\max.}$ (m μ)
Co py ₂ Cl ₂	CHCl ₃ soln.	—	579, 611, 638, ~662sh
"	MeNO ₂ "	—	580, 615, ~638sh
"	Pyridine "	0.45	505, 530, ~550sh
Co py ₂ Br ₂	CHCl ₃ "	—	597, ~636sh, 647
"	Pyridine "	0.30	525, ~545sh, ~575sh
Co py ₂ I ₂	CHCl ₃ "	—	~628sh, 659, 685
"	MeNO ₂ "	24	~628sh, 659, 687, ~735sh
"	Pyridine "	27	520, 547, ~580sh
"	9 : 1 w/w MeNO ₂ -pyridine soln.	205	~470sh, 506, ~520sh
"	Solid	—	~620, 650, ~685
Co py ₂ (NCO) ₂	CHCl ₃ soln.	—	547, 581, 631, 654
"	Pyridine "	0.50	470—495, ~510sh
Co py ₂ (NCS) ₂	CHCl ₃ "	—	560, 595, 628, ~654sh
"	MeNO ₂ "	—	~570sh, 616
"	Pyridine "	0.55	500, 515sh, ~545sh
Co py ₂ NCSe ₂	CHCl ₃ "	—	562, 600, 625
"	MeNO ₂ "	—	~570sh, 611
"	Pyridine "	0.31	500, ~545sh
Co mp ₂ Cl ₂	CHCl ₃ "	—	~585sh, ~615sh, 637
"	Solid	—	580—640
Co mp ₂ Br ₂	CHCl ₃ soln.	—	~600sh, ~630sh, 658
"	Solid	—	590—670
Co mp ₂ I ₂	CHCl ₃ soln.	—	~625sh, 660, 690
"	Solid	—	600—700
Co mp ₂ (NCO) ₂	CHCl ₃ soln.	—	552, 590, 625, ~650sh
"	Solid	—	550, ~595, ~620, ~650sh
Co mp ₂ (NCS) ₂	CHCl ₃ soln.	—	~565sh, ~605sh, 620
"	Solid	—	550—630
Co mp ₂ (NCSe) ₂	CHCl ₃ soln.	—	~568sh, 610
"	Solid	—	560—620
[Co py ₆][NO ₃] ₂	Pyridine soln.	17	~470sh, 506, ~520sh

Py = pyridine, mp = 2-methylpyridine.

Molar extinction coefficients fall in the range 300—1000 for the chloroform solution spectra and the range 3—10 for the pyridine solution spectra.

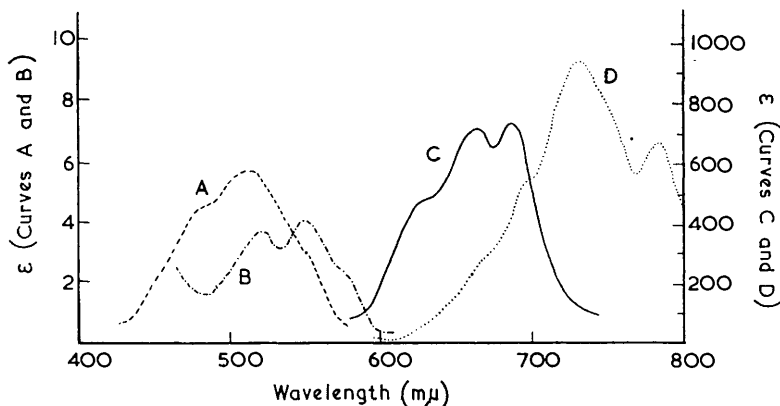


FIG. 1. Spectra of Co py₂I₂ in various solvents.

(A) 1 : 9 w/w Pyridine-nitromethane (identical with [Co py₆][NO₃]₂ in pyridine). (B) Pyridine. (C) Chloroform. (D) CoI₄²⁻ ([Ph₃MeAs][CoI₄] in nitromethane; Gill and Nyholm, *J.*, 1959, 3997).

and one at 597 m μ . The former is due to the pyridine adduct, Co py₄Br₂, and the latter to the tetrahedral molecule, Co py₂Br₂. However, because of the very great difference in the molar extinction coefficients of the two species and the overlap between the bands, the peak at 525 m μ appears to fall in intensity as the pyridine content is increased whereas it

would be expected to rise. This apparent fall in intensity is due to decrease in the overlap component from the stronger 597 m μ band, as the pyridine concentration increases; in fact, the absorption (at 525 m μ) due to the adduct actually increases. For example, it is clear that the relative intensities of the two bands are very different in any two curves. Because of the large difference in the extinction coefficients it was not possible experimentally to obtain completely resolved spectra (of sufficient optical density) for both species for all values of the pyridine : Co py₂Br₂ ratio.

(3) With one exception, the complexes all gave electrically non-conducting solutions in chloroform, nitromethane, or pyridine, or in mixtures thereof. The iodide Co py₂I₂ was exceptional in that, although the chloroform and chloroform-pyridine solutions used in the equilibrium measurements were non-conducting, a molar conductance of 27 mho (10⁻³M-solution) was observed with pure pyridine. This rather high value is believed to be due to labile iodide ions rather than to a disproportionation such as reaction (3) since the spectrum in the same solvent accords with the view that it arises from the complex Copy₄I₂ and

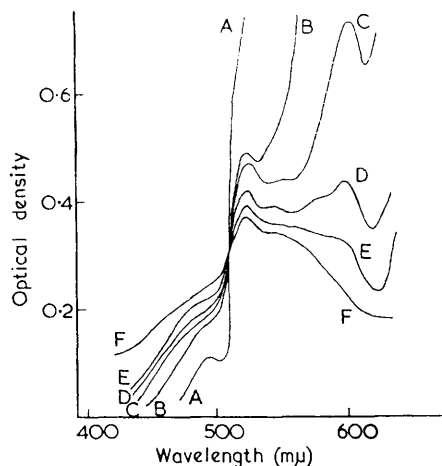


FIG. 2. Isobestic point for spectra of Co py₂Br₂ in chloroform-pyridine solutions ($\sim 0.03M$).

(A) No added pyridine. (B-F) Pyridine:Co py₂Br₂ (moles), (B) 24.7, (C) 43.7, (D) 58.3, (E) 67.0, (F) 80.7.

not the ion Co py₆²⁺ (compare curves A and B, Fig. 1). In nitromethane containing 10% by weight of pyridine, on the other hand, the spectrum (curve A, Fig. 1) and the high conductance ($\Lambda_M = 205$ mho) both point to extensive decomposition.

(4) The reflectance spectra, where measured, of those complexes which are tetrahedral in the solid state corresponded well with the 580-680 m μ spectra of chloroform and chloroform-pyridine solutions.

TABLE 2.

Thermodynamic data for the tetrahedral-octahedral equilibria in chloroform solution at 20°. (*K* values in parenthesis denote measurements in nitromethane.)

Complex	<i>K</i>	$-\Delta F$ (kcal. mole ⁻¹)	$-\Delta H$ (kcal. mole ⁻¹)	$-\Delta S$ (cal. deg. ⁻¹ mole ⁻¹)
Co py ₂ Cl ₂	12.6 (0.40)	1.48 \pm 0.02	15.2 \pm 0.2	46.8 \pm 0.7
Co py ₂ Br ₂	9.04	1.28 \pm 0.02	15.6 \pm 0.2	48.8 \pm 0.8
Co py ₂ I ₂	2.32	0.49 \pm 0.03	16.6 \pm 0.2	54.9 \pm 0.9
Co py ₂ (NCO) ₂ ...	23.3	1.83 \pm 0.03	13.7 \pm 0.2	40.5 \pm 0.8
Co py ₂ (NCS) ₂	83,000 (3550)	6.60 \pm 0.04	16.6 \pm 0.3	34.1 \pm 1.0
Co py ₂ (NCSe) ₂ ...	$\geq 100,000$ (27,800)	(Insufficiently soluble for precise measurement)		

Thermodynamic functions for the equilibrium (1) are given in Table 2 for all the pyridine complexes in chloroform solution and for some in nitromethane solution. The complexes can be divided into two groups: (a) the halides and the cyanate having a small tendency to co-ordinate two additional molecules of pyridine (*K* < 25); and (b) the thiocyanate and selenocyanate which have equilibrium constants several orders of

magnitude greater. No precise values are given for the 2-methylpyridine complexes because with these the equilibrium lies very far to the left. Indeed, the halides showed little or no tendency to co-ordinate further, even in solution in the parent amine itself. With the thiocyanate a small but definite tendency to form the octahedral complex was observed although K was still much too small for accurate measurement; a very rough estimate is $K = \sim 10^{-6}$. Since the basicities of pyridine and its 2-methyl derivative are very similar ($pK_a = 5.23$ and 5.97 , respectively ⁷), it seems clear that the methyl group in the α -position imposes a serious steric barrier to the formation of the CoL_4X_2 complex. It is interesting, too, that the large difference in the effects of halide and thiocyanate, observed for $L = \text{pyridine}$, is apparently maintained for $L = 2\text{-methylpyridine}$. Attempts to isolate complexes of the type, $\text{Co mp}_4\text{X}_2$, in the solid state failed (mp = 2-methylpyridine). This conflicts with the claim by Bhattacharya and Sinha ¹⁰ to have prepared a complex $\text{Co mp}_4(\text{NCS})_2$ by recrystallising cobalt thiocyanate from 2-methylpyridine. The corresponding 3-methyl and 4-methyl compounds are, however, readily formed,⁶ so presumably the amine used by these workers was impure.

On first inspection it seems that the relatively small differences in K between the three halide complexes might be accountable in terms of an increasing polarisability in the sequence $\text{Cl} < \text{Br} < \text{I}$ (as Gill *et al.*³ suggested from a consideration of the preferred co-ordination number in the solid) or in terms of steric factors. However, neither explanation accounts for the very different behaviour of the thiocyanate and selenocyanate complexes or of the difference between these and the cyanate analogue. In all three pseudohalide complexes it is known from visible and infrared spectral data that bonding to the metal is through the nitrogen atom,^{5,9} so even if we allow that the polarisability of, say, thiocyanate, is substantially less than that of chloride there is no *a priori* basis for believing it to be less than that of cyanate; the effect seems unaccountably large when compared with the relatively small effect produced by replacing chloride by bromide or iodide. An interpretation in terms of steric factors is equally unsatisfactory.

Enthalpies and Entropies of Reaction.—Table 2 shows that the large variations in K are determined mainly by entropy, and not by enthalpy, factors. Thus, for the thiocyanato- and the iodo-complex, the heat terms are the same within experimental error, so that here the responsibility for the fall in K from 83,000 to 2.32 rests entirely on the entropy term. Negative entropies of the observed order of magnitude are to be expected in a system in which two of the three reacting species lose independent translational freedom. Similar values have been obtained previously for the association of some square-planar nickel(II) complexes with pyridine and its derivatives in benzene.⁷ No doubt solvation accounts in part for the actual observed values but these are thought to be relatively unimportant because, first, no charged species is present and, secondly, chloroform is a fairly non-coordinating solvent. Of the three molecular species involved in the reaction the free amine is the one expected to be solvated most strongly, probably as a result of hydrogen-bonding.¹¹ This solvation, such as it may be, is likely to break down once the amine is co-ordinated to the tetrahedral complex. While this will make the entropy change more positive the effect will be a constant one since pyridine is the amine in all the equilibria considered. Therefore, to account for the differences in ΔS (~ 2 – 21 e.u.) between the reactions, it is proposed that, in addition to the substantially constant loss of translational entropy, there is a loss of rotational entropy on formation of the octahedral complex, to an extent governed by the nature of the anionic ligand X. This is regarded as arising from some potential barrier to rotation of the co-ordinated pyridine molecules about the metal–nitrogen bond as a result of steric interactions or multiple bonding. While some limitation to free rotation of pyridine ligands must exist in all the octahedral complexes, steric factors alone cannot be responsible for the dependence of ΔS on X. This must be true even in the case

¹⁰ Bhattacharya and Sinha, *J. Indian Chem. Soc.*, 1955, **32**, 414.

¹¹ Pimentel and McClellan, "The Hydrogen Bond," Freeman and Co., San Francisco, 1960, p. 197.

of the halides, where decreasing rotational freedom with increasing size of the halide ion is to be expected, since $-\Delta H$ increases in the same sequence; it seems that the metal-pyridine bond is strongest in the iodo-complex, a conclusion in conflict with purely steric arguments. Again, the much more positive entropy change (-34.1 e.u.) for the complex $\text{Co py}_2(\text{NCS})_2$ than for its analogue $\text{Co py}_2(\text{NCO})_2$ (-40.5 e.u.) cannot be explained on steric grounds. Double bonding between cobalt and pyridine is therefore indicated. This is possible since in an octahedral field spin-free cobalt(II) has an almost filled t_{2g} non-bonding shell capable of overlap with vacant anti-bonding π -orbitals of pyridine. Dative π -bonding in metal-pyridine bonds have been postulated previously,⁷ but our results suggest that the extent of the $d\pi-p\pi$ overlap is strongly influenced by the nature of the anionic ligand partner. In Table 2 the order of effectiveness in inducing π -bonding is: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NCO}^- > \text{NCS}^- > \text{NCSe}^-$.

It is of interest to compare the observed difference in ΔS between pairs of reactions with the value calculated on the assumption of complete loss of rotation of a pyridine molecule about the metal-nitrogen bond. The rotational entropy for this axis of rotation is given¹² by

$$S_{\text{rot}} = NkT \frac{d \ln Q_{\text{rot}}}{dT} + kN \ln Q_{\text{rot}},$$

where the partition function (Q_{rot}) is $\frac{1}{2}(8\pi^2IkT/h^2)^{\frac{1}{2}}$. The moment of inertia (I) of the pyridine molecule about the rotational axis in question was calculated from its atomic dimensions.¹³ S_{rot} was found to be 7.7 e.u. per pyridine at 20° . Now, even if it is assumed that in the reaction of the iodo-complex (for which ΔS is the most negative) the two reacting pyridine molecules lose all their rotational freedom on co-ordination, and that in the thiocyanate (having the least negative entropy of association) no rotational freedom is lost, we should expect a ΔS difference of about 15.4 e.u., whereas the observed difference is 20.8 e.u. This suggests we should consider the rotational loss of four pyridine molecules, and not just the two incoming ones. In this case the maximum possible entropy loss is ~ 31 e.u., a value in excess of that observed, as required. This picture, which assumes little or no π -bonding in the tetrahedral complex, seems reasonable when it is remembered that in a tetrahedral configuration the non-bonding metal d -orbitals have a less favourable symmetry for overlap with ligand π -orbitals than in the octahedral complex in which the ligands are in orthogonal relationship. It has been assumed in this calculation that vibrational-entropy contributions and any changes which take place in other parts of the molecule are relatively unimportant.

The influence of the anionic ligand X can now be discussed in terms of electronic effects transmitted to the metal-pyridine bond by means of metal orbitals. When X is easily polarisable, *e.g.*, I^- , charge is readily transferred to the metal along the σ -bond, thereby lowering its effective electron affinity towards other ligands. If the effect were purely inductive, $-\Delta H$ should fall in the sequence $\text{Cl}^- > \text{Br}^- > \text{I}^-$, the entropy term remaining relatively unaffected. In fact, the opposite is observed and it is suggested, therefore, that the effect of increasing charge transfer from X to metal is to enhance the release of non-bonding metal d -electrons to anti-bonding pyridine π -orbitals, thereby raising the bond order of the metal-pyridine bond. The much more positive ΔS found for the thiocyanate is clearly not a polarisability effect and may be understood rather in terms of a measure of dative π -bonding ($d\pi \longrightarrow p\pi$) in the Co-NCS bond, which renders the non-bonding metal orbitals less available for overlap with pyridine π -orbitals. Cyanate ion seems to be a less effective π -acceptor than thiocyanate; and although entropy data are not available for the selenocyanate complex the high negative free-energy changes in both chloroform and nitromethane solution suggest an even greater π -acceptor capacity than for thiocyanate.

Some independent evidence for a measure of double-bonding in metal-thiocyanate

¹² Davidson, "Statistical Mechanics," McGraw-Hill, New York, 1962.

¹³ Sutton *et al.*, "Interatomic Distances," *Chem. Soc. Spec. Publ.* No. 11, 1958.

bonds is available. For example, Chamberlain and Bailar¹⁴ account for the lower CN stretching frequency in co-ordinated NCS, compared with that in organic nitriles, as a reflection of a loss of triple-bond character with a consequent gain in metal-nitrogen bond order. Also, thiocyanate is known to be a good *trans*-directing ligand in certain substitution reactions, which according to Chatt and his co-workers is an indication of some double-bonding with the central metal atom.¹⁵ It should be added, however, that in the palladium(II) and platinum(II) complexes in which the *trans*-directing influence has been assessed the bonding is probably through the sulphur,¹⁶ and not through the nitrogen atom as in the complexes considered here.

The Solid Complexes.—While all the bisamine complexes assume a tetrahedral configuration in non-decomposing solvents, in the solid state some exist in a polymeric octahedral form (see Table 3). The structures of the pyridine compounds have been determined previously,³⁻⁵ but those of the methyl-substituted analogues have not. Structural assignments are made on the basis of magnetic moment and the position and intensity of the visible bands of the solid-state spectra (see Tables 1 and 3).

TABLE 3.

Complex	Colour	Magnetic moment (B.M.)	Temp.	Stable confign. of solid	<i>K</i> (CHCl ₃ solution)
Co py ₂ Cl ₂ (α -form)	Violet	5.15 ³	20°	Bridged octahedral	12.6
Co py ₂ Br ₂	Blue	4.50 ³	20	Tetrahedral	9.04
Co py ₂ I ₂	Green	4.47 ³	20	"	2.32
Co py ₂ (NCO) ₂	Blue	4.48 ⁵	18	"	23.3
Co py ₂ (NCS) ₂	"	5.11 ⁵	18	Bridged octahedral	83,000
Co py ₂ (NCSe) ₂ ...	Green-brown	5.14 ⁵	18	"	≥100,000
Co mp ₂ Cl ₂	Blue	4.48	16.5	Tetrahedral	Immeasurably small
Co mp ₂ Br ₂	"	4.56	15.8	"	"
Co mp ₂ I ₂	Green	4.61	17.5	"	"
Co mp ₂ (NCO) ₂ ...	Blue	4.62	16.2	"	"
Co mp ₂ (NCS) ₂	"	4.47	17.5	"	~10 ⁻⁶
Co mp ₂ (NCSe) ₂ ...	Blue-green	4.41	17.5	"	Decomp.

The thermodynamic results for solution behaviour of the complexes permit a new evaluation of the factors responsible for the adoption of a particular configuration in the solid state. Where there is no steric hindrance to the attainment of six-co-ordination the equilibrium constant *K* is a sensitive indicator of the degree of co-ordinative unsaturation of the metal in the tetrahedral environment in solution. In general, there is a good correlation between *K* and solid-state configuration. The bromo- and the iodo-pyridine complexes, which have the lowest *K* values, are tetrahedral in the solid, and the thiocyanato- and the selenocyanato-complexes, which have very high *K* values, are six-co-ordinate. However, there is a reversal in the expected configurations of the chloro- and cyanato-complexes. A possible reason for this anomaly is a reluctance on the part of cyanate to co-ordinate through its oxygen atom, dual linkage being a requirement for the formation of an octahedral complex.⁵ Support for this view is provided by the apparent non-existence of the normal form (R·OCN) of organic cyanates, whereas organic thiocyanates are known in both the normal (R·SCN) and the iso-form (R·NCS).¹⁷ Moreover, we have been unable to prepare the cyanate analogue of the complexes Co(NCS)₄Hg¹⁸ and Co(NCSe)₄Hg¹⁹ which have been shown by X-ray analysis to contain bridging SCN⁻ and SeCN⁻ groups. It seems that cyanate can be induced to adopt a bifunctional co-ordinating role only when the other ligand partners have a poor σ -donor (or high π -acceptor) capacity, *e.g.*, 4-cyanopyridine,

¹⁴ Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412.

¹⁵ Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456.

¹⁶ Mitchell and Williams, *J.*, 1960, 1912.

¹⁷ Sidgwick, "Chemical Elements and their Compounds," Oxford, 1950, p. 674.

¹⁸ Jeffrey, *Nature*, 1947, **159**, 610.

¹⁹ Cotton, Goodgame, Goodgame, and Haas, *Inorg. Chem.*, 1962, **1**, 565.

rendering the metal unsaturated in the 4-co-ordinate condition in the terms of reference of the electroneutrality principle.²⁰

As expected from the negligible tendency of the 2-methylpyridine complexes to associate with free amine in solution, the solid-state structure is tetrahedral, even when X = SCN or SeCN.

It is noteworthy that while our free-energy values for solution equilibria confirm the interpretation by Gill *et al.*³ of the structure of the dipyridine halides, the entropy values indicate that the mechanism of operation of the electroneutrality principle in complexes of this kind is not necessarily a simple inductive one, but that it may involve also important mesomeric interactions between the central acceptor atom and all the atoms or groups attached to it.

Nickel(II) Complexes.—It is of interest to compare the structures of the cobalt complexes discussed above with those of corresponding nickel compounds. The higher crystal-field stabilisation in an octahedral field, and the lower stabilisation in a tetrahedral field, for the d^8 -ion than for a d^7 -ion, renders the occurrence of tetrahedral complexes less likely with nickel than with cobalt. We predict, therefore, that in complexes of the type NiL_2X_2

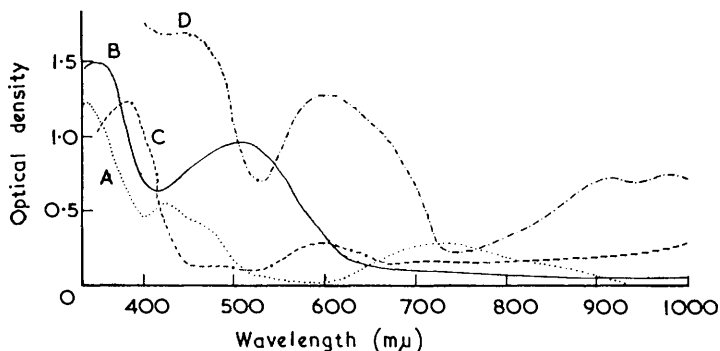


FIG. 3. Reflectance spectra of nickel(II) complexes.

(A) $Ni py_2Br_2$. (B) $Ni mp_3(NCS)_2$. (C) $Ni py_2(NCS)_2$. (D) $Ni py_2I_2$.

there should be a greater driving force for the adoption of a polymeric octahedral structure. Of the dipyridinenickel halides, only the chloride and iodide seem to have been structurally characterised. $Ni py_2Cl_2$ is said to be isostructural with the violet form of the cobalt compound $Co py_2Cl_2$ and therefore to be an octahedral polymer;³ and recently, the iodide $Ni py_2I_2$ has been assigned a tetrahedral structure on the evidence of its visible and infrared spectra.²¹ In each case the configuration is the same as that of the corresponding cobalt complex, although the chloride $Co py_2Cl_2$ exists also in a metastable tetrahedral form not evident with $Ni py_2Cl_2$. It was of particular interest, therefore, to examine the complex $Ni py_2Br_2$, the cobalt analogue being four-co-ordinate. A magnetic moment of 3.30 B.M. at 18° was found and although this value falls in the expected range (2.83—~3.4 B.M.) for six-co-ordinate nickel(II) and below the range (3.5—4.2 B.M.) usually associated with regular tetrahedral co-ordination,²² it does not rule out the possibility of a distorted tetrahedral structure, as indeed seems indicated for the iodide $Ni py_2I_2$ from the low value of the moment (Table 4). However, the electronic spectrum of the compound $Ni py_2Br_2$ (Fig. 3) is consistent only with the metal's having an octahedral ligand field, though possibly tetragonally distorted;²³ the bands are much weaker than those required

²⁰ King, Körös, and Nelson, *Nature*, 1962, **196**, 572.

²¹ Glonek, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1962, **84**, 2014.

²² Cotton and Wilkinson, "Advanced Inorganic Chemistry," Interscience Publ., Inc., New York, 1962, p. 738.

²³ Maki, *J. Chem. Phys.*, 1958, **28**, 651; 1958, **29**, 102.

for a tetrahedral configuration (see Fig. 3). The six-co-ordination of the metal in this compound, as against four-co-ordination in the cobalt analogue $\text{Co py}_2\text{Br}_2$, is thus in accord with ligand-field predictions.

TABLE 4.

Complex	Colour	Magnetic moment (B.M.)	Temp.	Confign.
$\text{Ni py}_2\text{Cl}_2$	Yellow-green	3.37 ³	20°	Bridged octahedral
$\text{Ni py}_2\text{Br}_2$	Yellow	3.30	18	"
$\text{Ni py}_2\text{I}_2$	Dark green	3.44 ²¹	~20	Tetrahedral
$\text{Ni py}_2(\text{NCS})_2$	Blue-green	3.26	19	Bridged octahedral
$\text{Ni mp}_2(\text{NCS})_2$	Red	Diamagnetic		Planar

It is noteworthy that while the bromo-complex $\text{Ni py}_2\text{Br}_2$ has low solubility in most organic solvents, a reflection of the polymerised nature of the lattice, the iodo-analogue $\text{Ni py}_2\text{I}_2$ is, in contrast, freely soluble, as would be expected for a molecular compound of discrete tetrahedral constitution. The close correspondence of the solid state (Fig. 3) and chloroform solution spectra in the visible and near-infrared regions indicate that the iodide dissolves without decomposition, in this solvent at least. On addition of a small amount of pyridine the colour immediately changes from intense green to pale yellow. The electronic spectrum of this yellow solution is identical with that of the solid material $\text{Ni py}_4\text{I}_2$.⁶ This is the first example of a simple tetrahedral-octahedral configuration equilibrium in solution that we have encountered for nickel(II). The thermodynamic investigation of this equilibrium, now in progress, will, we hope, permit quantitative comparison of the relative co-ordinate unsaturation of Ni^{2+} and Co^{2+} in similar tetrahedral environments.

Replacement of pyridine by its 2-methyl derivative in cobalt complexes causes the six-co-ordinate state to be thermodynamically unstable. The same would be expected for nickel complexes and, indeed, Glonek *et al.*²¹ claim that the complexes $\text{Ni mp}_2\text{Cl}_2$ and $\text{Ni mp}_2\text{Br}_2$ are tetrahedral. However, in view of the preference of nickel(II) for octahedral co-ordination it seemed possible that the relatively high π -acceptor capacity of thiocyanate might induce the metal to attain six-co-ordination in spite of the severe steric restrictions imposed by the 2-methyl group. In fact, we found the red compound, $\text{Ni mp}_2(\text{NCS})_2$, to be diamagnetic. A square-planar structure is therefore indicated, and this is supported by the electronic spectrum (Fig. 3) which is similar to those of other nickel complexes of known planar configuration.²⁴ This complex may be compared with the corresponding pyridine compound $\text{Ni py}_2(\text{NCS})_2$ which on the evidence of its electronic spectrum (Fig. 3), moment (Table 4), and insolubility in organic solvents must be considered an octahedral polymer. It seems that, when six-co-ordination is prohibited for steric reasons, of the two possible four-co-ordinate configurations the planar alternative may sometimes be preferred, the choice depending, presumably on the strength of the ligand field.

EXPERIMENTAL

Preparation of the dipyridinecobalt complexes has been described.^{3,5}

Dichlorodi-(2-methylpyridine)cobalt(II).—A hot ethanolic solution of hydrated cobalt chloride (1 mol.) was mixed with a hot ethanolic solution of 2-methylpyridine (~2.5 mol.). On cooling, blue crystals separated. The product was recrystallised from ethanol, washed with cold carbon tetrachloride, and dried in air [Found: Co, 18.6. $\text{Co}(\text{C}_6\text{H}_7\text{N})_2\text{Cl}_2$ requires Co, 18.6%].

Dibromodi-(2-methylpyridine)cobalt(II) was prepared analogously [Found: Co, 14.6. $\text{Co}(\text{C}_6\text{H}_7\text{N})_2\text{Br}_2$ requires Co, 14.6%].

Di-iododi-(2-methylpyridine)cobalt(II).—Ethanolic solutions of hydrated cobalt nitrate (1 mol.) and potassium iodide (2 mol.) were mixed and the precipitated potassium nitrate was filtered off. The solution was evaporated to small bulk under an infrared lamp, then filtered,

²⁴ Coussmaker, Hely-Hutchinson, Mellor, Sutton, and Venanzi, *J.*, 1961, 2705; Browning *et al.*, *J.*, 1961, 4816; 1962, 693; Goodgame and Goodgame, *J.*, 1963, 207.

and the amine (2.5 mol.) was added. Green crystals slowly separated. This complex was purified by recrystallisation from ethanol [Found: Co, 11.9. $\text{Co}(\text{C}_6\text{H}_7\text{N})_2\text{I}_2$ requires Co, 11.8%].

Dicyanatodi-(2-methylpyridine)cobalt(II).—Cold aqueous-ethanolic solutions of hydrated cobalt nitrate (1 mol.) and potassium cyanate (2 mol.) were mixed and the amine (~2.5 mol.) was added. The blue crystalline complex which separated on storage was recrystallised from ethanol [Found: Co, 18.0. $\text{Co}(\text{C}_6\text{H}_7\text{N})_2(\text{NCO})_2$ requires Co, 17.9%].

Dithiocyanatodi-(2-methylpyridine)cobalt(II) was prepared analogously to the di-iodo-complex [Found: Co, 16.3. $\text{Co}(\text{C}_6\text{H}_7\text{N})_2(\text{NCS})_2$ requires Co, 16.3%]; so was *diselenocyanatodi-(2-methylpyridine)cobalt(II)* [Found: Co, 13.0. $\text{Co}(\text{C}_6\text{H}_7\text{N})_2(\text{NCSe})_2$ requires Co, 13.0%].

Dibromodipyridinenickel(II).—A hot ethanolic solution of hydrated nickel bromide (1 mol.) was mixed with one of pyridine (~1.8 mol.). A blue solution was formed and gave almost immediately a yellow microcrystalline precipitate. The product was washed with hot ethanol and dried in air [Found: Ni, 15.7. $\text{Ni}(\text{C}_5\text{H}_5\text{N})_2\text{Br}_2$ requires Ni, 15.6%].

Di-iododipyridinenickel(II).—The method of preparation described by Glonek *et al.*²¹ was employed [Found: Ni, 12.5. Calc. for $\text{Ni}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$: Ni, 12.5%].

Dithiocyanatodipyridinenickel(II).—To hot aqueous nickel nitrate (1 mol.) were added pyridine (~1.8 mol.) and warm aqueous potassium thiocyanate (2 mol.). The green complex produced was washed with hot water and hot ethanol and dried in air [Found: Ni, 17.8. Calc. for $\text{Ni}(\text{C}_5\text{H}_5\text{N})_2(\text{NCS})_2$: Ni, 17.6%].

Dithiocyanatodi-(2-methylpyridine)nickel(II).—Ethanolic solutions of hydrated nickel nitrate (1 mol.) and potassium thiocyanate (2 mol.) were mixed and the precipitated potassium nitrate was filtered off. The filtrate was evaporated to small volume and filtered again, and 2-methylpyridine (~2.5 mol.) was added. Slow evaporation under an infrared lamp was continued until the red product crystallised. Visible decomposition occurred in all solvents tried and recrystallisation was not therefore possible [Found: Ni, 16.0. Calc. for $\text{Ni}(\text{C}_6\text{H}_7\text{N})_2(\text{NCS})_2$: Ni, 16.3%].

Measurement of Equilibrium Constants.—These were carried out spectrophotometrically by a method similar to that described by Sacconi *et al.*⁷ Chloroform used as solvent was of "AnalaR" quality, dried (Na_2SO_4), and distilled before use. Nitromethane (B.D.H.) was treated similarly. The spectrophotometer was an "Optica" double-beam recording model. To obtain K , a series of solutions of the complex, of the same accurately known concentration (~ 10^{-3}M), were prepared containing different known amounts of pyridine. The equilibrium concentration of the tetrahedral species in each was determined by reference to a previously determined calibration curve relating $[\text{Co py}_2\text{X}_2]$ to optical density. K was calculated from the equation $K = x/(A - x)(B - 2x)^2$, where x is the equilibrium concentration of the octahedral adduct and A and B are the initial concentrations of the tetrahedral complex and pyridine, respectively. The temperature of measurement was $20^\circ \pm 0.5^\circ$. Errors in ΔF are estimated to be of the order of 20–40 cal. For example, in five determinations, K for the $\text{Co py}_2\text{Cl}_2$ reaction was 12.17, 12.60, 13.03, 12.22, and 12.97. The maximum deviation about the mean value (12.60) is ± 0.43 , *i.e.*, about $\pm 3.5\%$. This corresponds to an uncertainty in ΔF of about ± 20 cal.

Calorimetric Measurements.—A calorimeter similar to that described by Davies, Singer, and Staveley²⁵ was used. Differences were the use of a thermistor (Stantel, type F22) for the detection of temperature changes and a 1-mv potentiometric recorder for automatic recording of the temperature pattern during a run. A thin-walled glass bulb, containing a weighed amount of the dipyridine complex, was broken under the surface of the solvent (600 ml.) by allowing it to come in contact with the double-bladed glass stirrer. Calibrations for each run were carried out electrically by means of a 32.2-ohm heater of 24-gauge constantan wire encased in a spiral of thin-walled Pyrex tubing filled with Silicone oil. The calorimeter was immersed in a water-thermostat-bath at $20^\circ \pm 0.1^\circ$. Two heats of solution of the dipyridine complex were required for each determination of ΔH , one in chloroform and another in chloroform containing a known excess of pyridine. Percentage reactions were calculated from the equilibrium constants determined previously. ΔH values listed in Table 2 are the averages of several determinations in each case. Errors were governed mainly by the solubility, and rate of dissolution, of the complex under study.

Other Physical Measurements.—Magnetic moments were determined by the Gouy method at room temperature. The material $\text{Hg}(\text{SCN})_4\text{Co}$ was used as the calibrating substance.

²⁵ Davies, Singer, and Staveley, *J.*, 1954, 2304.

Reflectance spectra were obtained with a Hilger Uvispek spectrophotometer, type H 700, fitted with a reflectance attachment of type H 740.

Electrical conductances were measured with an RC bridge, fitted with a CR tube null detector, at frequencies in the range 0.3—10 kc. sec.⁻¹.

One of us (E. K.) acknowledges grant of study leave from the L. Eötvös University of Budapest, and a Research Fellowship from the Queen's University of Belfast.

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[Received, April 30th, 1963.]
