Complex Formation between the Hydrogen Ion and Cobalt(II), Nickel(II), Copper(II), Zinc(II), Silver(I), and Cadmium(II) Ions and 2-Substituted Pyridines containing Unsaturated Side Chains

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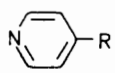
A number of substituted pyridines containing unsaturated substituents in the 2-position have been synthesised and the formation constants of their complexes with the hydrogen ion, silver(I), and cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) ions have been measured at 25 °C and $I = 0{\cdot}10$M (KNO_3). Chelate formation takes place between Ag^+ and ligands with olefinic bonds two or more atoms removed from the nitrogen atom, with a preference for chelate rings which are ' five and one half membered '.

As a ligand, pyridine (py) forms many stable complexes with transition-metal ions, the nitrogen atom acting as the donor centre. In particular it forms stable complexes with Ag^+ ions showing definite ' soft ' behaviour. Complexes of many different C-substituted pyridines, with the substituents in the 3- or 4-positions, have been studied and attempts made to correlate electronic effects of the substituent groups with the type of metal–ligand bonding present.[1,2] If the substituents are in the *ortho*-position, steric interaction prevents reliable correlation using free-energy relations. In addition, if the side chain has any donor properties making chelate formation possible, interaction will tend to be far greater than the effects of steric hindrance. In this investigation we have synthesised a range of 2-substituted pyridines, L, with olefinic bonds in the substituent groups. Olefinic bonds are known to be very ' soft ' donor centres and, since the py nitrogen atom is itself ' soft ' in character, the co-ordinating ability of the olefinic bond towards soft or class (b) metals such as Ag^+ should be enhanced considerably. This enhancement has been clearly demonstrated with ligands containing olefinic bonds and sulphur or selenium donor atoms able to form chelate complexes.[3]

The ligand (L; R = Pr^n) was prepared for comparison since it has similar steric properties but is unable to co-ordinate through the side chain. Pyridine was studied to obtain results under identical experimental conditions. Results for [L = $Me{\cdot}CH(OH){\cdot}CH_2$ and $Ph{\cdot}CH(OH){\cdot}CH_2$] are included since these compounds were obtained in the

(L) R = H, $H_2C{:}CH$, $H_2C{:}CH{\cdot}CH_2$, $H_2C{:}CH{\cdot}CH_2{\cdot}CH_2$, $H_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$, Pr^n, $Me{\cdot}CH(OH){\cdot}CH_2$, $Ph{\cdot}CH(OH){\cdot}CH_2$, $HO{\cdot}OC{\cdot}HC{:}CH$, and 2-py·$HC{:}CH$

pure form as intermediates in the synthetic work. In addition, two ligands, L', substituted in the 4-position



(L') R = $H_2C{:}CH$ or 4-py·$HC{:}CH$

were also studied. These ligands are unable to chelate effectively to a single metal ion but could act as multidentate ligands by forming polynuclear complexes. In all cases, protonation constants for the ligand were measured together with formation constants for complexes of the bivalent ions Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, and Cd^{2+}, and for Ag^+.

EXPERIMENTAL

Preparation of Ligands.—The unsaturated pyridines were prepared by methods based on those of Troyansky [4] and

[1] J. J. R. Frausto Da Silva and J. G. Calado, *J. Inorg. Nuclear Chem.*, 1966, **28**, 125.
[2] M. S. Sun and D. G. Brewer, *Canad. J. Chem.*, 1967, **45**, 2729.
[3] L. D. Pettit and C. Sherrington, *J. Chem. Soc.* (*A*), 1968, 3078.
[4] C. Troyansky, *Bull. Soc. chim. France*, 1955, 420.

Marvel *et al.*[5] Representative preparations are given in detail.

2-(*But-3-enyl*)*pyridine*. Lithium metal (3·5 g) in dry diethyl ether (200 cm³) was stirred under an inert atmosphere of dinitrogen while bromobenzene (40 g) in ether (50 cm³) was added at such a rate as to maintain gentle refluxing. The mixture was heated under reflux for 1 h, then freshly distilled 2-methylpyridine (25 g) in dry diethyl ether (50 cm³) was added. The resulting mixture was allowed to stand for 1 h, cooled, and the solution slowly become red due to formation of 2-pyridylmethyl-lithium. To the cold solution of the latter in diethyl ether was added allyl bromide (32 g) over 20 min. The mixture was heated under reflux with stirring for 1 h, and then hydrolysed by the addition of ice-cold 2M-ammonium chloride solution (200 cm³).* The ether layer was separated, washed with water, and dried over anhydrous sodium sulphate. Diethyl ether was removed by flash distillation and the oil so produced distilled at reduced pressure. 2-*n-Propylpyridine* and 2-(*pent-4-enyl*)*pyridine* were prepared similarly, using ethyl bromide and 4-bromobut-1-ene respectively in place of allyl bromide.

2-*Allylpyridine*. This compound was prepared from allylmagnesium bromide (0·4 mol) in diethyl ether and 2-bromopyridine (16 g). The mixture was heated under reflux for 1 h, hydrolysed for 1 h, then hydrolysed with water, and the diethyl ether layer removed. The aqueous layer was extracted with diethyl ether and the combined ether extracts dried over sodium hydroxide pellets. Diethyl ether was removed and the dark brown oil fractionated under reduced pressure. A fraction was collected between 60 and 70 °C at 12 mmHg and was redistilled to yield a clear colourless liquid.

2-*Vinylpyridine*. 2-Pyridylmethyl-lithium (0·25 mol) in diethyl ether was stirred while formaldehyde gas (prepared by heating the polymer at 190 °C) was passed over the surface of the solution. When the red colour of the solution was discharged, the mixture was hydrolysed with 2M-ammonium chloride solution (100 cm³). The diethyl ether layer was removed, and the aqueous layer extracted repeatedly with small volumes of ether. The combined ether layers were dried over anhydrous sodium sulphate, the ether distilled off, and the resulting black oil fractionated under reduced pressure. This material was identified as 2-(1-hydroxyethyl)pyridine, yield 40%, b.p. 91 °C at 1 mmHg. This compound was dehydrated by addition of powdered potassium hydroxide (3·0 g) and quinol (0·1 g) and heating under distillation. The condensed vapours were fractionated under reduced pressure.

2-(2-*Hydroxypropyl*)*pyridine*. To 2-pyridylmethyl-lithium (0·25 mol) in diethyl ether was added acetaldehyde (11·0 g) in ether (50 cm³). The mixture was stirred at room temperature for 1 h and then poured over ice. The precipitated solid was dissolved by rapid agitation, the ether layer removed, dried over anhydrous sodium sulphate, and diethyl ether removed by flash distillation. The red oil obtained was fractionally distilled under reduced pressure. Attempts to dehydrate the alcohol by heating with potassium hydroxide proved unsuccessful.

2-[(*Hydroxybenzyl*)*methyl*]*pyridine*. 2-Pyridylmethyl-lithium (0·25 mol) in diethyl ether (100 cm³) was stirred at 0 °C while benzaldehyde (26·5 g) in ether (50 cm³) was added dropwise over 20 min. The mixture was heated under reflux for 1 h, cooled, and hydrolysed by the addition of iced ammonium chloride solution. The pasty yellow solid formed was filtered off and triturated with dichloromethane. A further yield of solid was obtained by separation of the ether layer and evaporation to small volume. The solid obtained was recrystallised from benzene–light petroleum (1 : 2). Again attempts to dehydrate the alcohol were unsuccessful, although the temperature was raised until charring began.

2-(*Carboxyvinyl*)*pyridine*. Malonic acid (10·5 g), 2-formylpyridine (10·6 g), and piperidine (0·1 g) were mixed and the solution cooled until the initial exothermic reaction ceased. The reaction was completed by warming the solution on a steam-bath for 20 min. The resulting dark brown solution was evaporated to dryness under reduced pressure and a brown solid remained. This was recrystallised from aqueous ethanol and then water with the aid of activated charcoal. The molecule, which exists in water as the zwitterion, has two geometric isomers, *cis* and *trans*. The ^{1}H n.m.r. spectrum in dimethyl sulphoxide (dmso) showed the product to be the *trans*-isomer.

Analyses and properties of the ligands synthesised are shown in Table 1. Other ligands used were purified samples of commercially available materials.

TABLE 1

Analytical data for *ortho*-substituted pyridines 2-RC_5H_4N, (L)

R	B.p., θ_c/°C (P/mmHg)	Analyses (%) * C	Analyses (%) * H	Yield (%)
$H_2C{:}CH$	42 (4)	80·2 (80·0)	6·8 (6·7)	35
$H_2C{:}CH{\cdot}CH_2$	62 (11)	80·4 (80·6)	8·2 (7·9)	42
$H_2C{:}CH{\cdot}CH_2{\cdot}CH_2$	72 (4)	81·1 (81·2)	8·3 (8·3)	73
$H_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	95 (10)	81·7 (81·6)	9·0 (8·8)	67
Pr^n	167 (740)	79·3 (79·5)	9·1 (9·2)	61
$Me{\cdot}CH(OH){\cdot}CH_2$	115 (6)	70·3 (70·1)	7·9 (8·0)	68
$Ph{\cdot}CH(OH){\cdot}CH_2$	108 †	78·2 (78·4)	6·7 (6·7)	91
$HO{\cdot}OC{\cdot}HC{:}CH$	205 †	64·5 (64·4)	4·5 (4·7)	66

* Calculated values are given in parentheses. † M.p.

Measurement of Protonation and Complex Formation Constants.—For the hydrogen ion and all metal ions other than Ag^+, formation constants were calculated from potentiometric-titration curves, obtained using a glass-indicator electrode and a mercury(II) sulphate reference electrode calibrated in terms of hydrogen-ion concentrations at 25 °C. Potentials were measured with a Radiometer PHM 64 digital pH meter. All solutions were made up in a background of KNO_3 (total I = 0·10M). When the ligand was prepared as the free base this was converted to the fully protonated form by adding the calculated amount of nitric acid. Titrations were carried out in a thermostatted vessel at 25 °C, alkali being added by means of a Radiometer ABU 12 automatic burette. Duplicate titrations were carried out with agreement always better than 0·007 pH units.

Titrations in the presence of silver were carried out by adding a solution of the ligand in an acetate buffer of pH 5·95 or 1·55, of total ionic strength 0·20M, to a solution of Ag^+ in the same buffer. During addition the potential of a Ag–AgCl indicator electrode was followed using a range of Ag : L ratios. In the low pH buffer the ligands are all fully protonated, hence complex formation can occur through the olefinic bond only. Such co-ordination was shown to be unimportant since results gave no indication of the formation of protonated complexes. In the high pH buffer the

* 1M = 1 mol dm^{-3}.

[5] C. S. Marvel, L. E. Coleman, and G. P. Scott, *J. Org. Chem.*, 1955, **20**, 1785.

ligands were partly protonated. Since it had been shown that the protonated form did not complex, the concentration of free base (readily calculated from the protonation constant and pH), was used in the calculations. To ensure maximum precision, the pH was recorded at each titration point, although the maximum variation found was 0·02 pH units. The protonated species HL^+ was therefore treated as an inert impurity in the titration mixture.

Complex-formation constants were calculated from the potentiometric data with the help of the MINIQUAD computer program.[6]

RESULTS AND DISCUSSION

Calculated formation constants for both protonation and metal complexes are given in Table 2. Silver complexes of the ligands (L; R = 2-py·HC:CH) and (L'; R = 4-py·HC:CH) were not studied because of sparing solubility in the pH 5·9 buffers. In general, complexes with the bivalent transition metal ions were weak; hence results calculated using the present procedure have comparatively low precision, as indicated in the Table. Standard deviations quoted refer to the variation in calculated constants in duplicate titrations. They do not allow for any systematic errors but should permit intercomparisons in Table 2 to the normally accepted limits of ± 2—3σ.

Protonation.—The vinylpyridines fell into the stability order 2-vinyl < py < 4-vinyl. Presumably steric hindrance in the *ortho*-substituted pyridine discourages protonation of the nitrogen atom, so making it less basic. Among the 2-substituted pyridines, the stability order was: 2-vinyl < py < 2-allyl < 2-(but-3-enyl) < 2-(pent-4-enyl) < 2-propyl. Only the 2-vinyl substituent can conjugate with the aromatic ring, so reducing the basicity of the nitrogen atom by its mesomeric effect. With all the other substituents the basicity increases as the chain length increases and the olefinic bond moves away from the ring, as would be expected from changes in inductive effects. Since the olefinic bond in 2-vinylpyridine is conjugated with the ring system the vinyl group will be coplanar with the ring, so introducing marked steric hindrance between a vinyl proton and a proton on the nitrogen atom [hence the low basicity of (L; R = H_2C:CH)]. Steric hindrance will be much less with other 2-substituted ligands since free rotation about the substituent–ring bond will be possible. Hence their basicities are less influenced by steric and more by electronic factors. For the alcohols [L; R = Me·CH(OH)·CH_2 and Ph·CH(OH)·CH_2] the stability order can also be explained in terms of different inductive effects.

2-(Carboxyvinyl)pyridine is a dibasic acid with a ratio of constants, $K_1 : K_2 = 59 : 1$. This supports the *trans*-configuration predicted by ^{1}H n.m.r. since it is close to the ratio for fumaric acid (36 : 1) and deviates considerably from that for maleic acid (*cis*) which is $4 \times 10^4 : 1$. By a similar argument, the (2-pyridylvinyl)pyridines are assigned the *trans*-configuration since the ratios $K_1 : K_2$ are 140 and 17 : 1 for the 2- and 4-substituted ligands respectively.

Silver(I) Complexes.—Values for formation constants of the silver–pyridine complexes were determined to ensure that comparisons were as valid as possible. Although conditions used were different from those of Sun and Brewer,[2] good relative agreement was found, *i.e.* log $\beta_1 = 1{\cdot}95$, log $\beta_2 = 3{\cdot}97$ compared to 2·12 and 4·25. None of the substituted pyridines studied showed any tendency to co-ordinate to silver when the pyridine nitrogen atom was protonated. Hence it can be assumed that the olefinic bonds cannot co-ordinate effectively unless aided by a chelate effect. For the vinylpyridines no evidence was found for olefin–silver bonding even at pH 5·9, since the stability order was the same as that for protonation and transition-metal-ion complex formation, *i.e.* 2-vinyl < py < 4-vinyl. Clearly chelation is not possible for steric reasons since the chelate ring would be only 'four and one half membered.' Similarly 2-(carboxyvinyl)pyridine gave no evidence of chelate formation. Since the molecule has been shown to be in the *trans*-configuration, chelation between the carboxyl group, nitrogen atom, and silver ion would be impossible also. The same argument applies to the (2-pyridylvinyl)-pyridine ligands which are also *trans* and, although of low solubility, showed no tendency to form stable silver complexes.

For the other 2-substituted pyridines the order of stability of the silver(I) complexes was: py < 2-allyl > 2-(but-3-enyl) > 2-(pent-4-enyl) > 2-propyl. Such a sequence can only be explained in terms of appreciable chelate formation, particularly with 2-allylpyridine which can form a 'five and one half membered' olefin–chelate ring. This has been shown to be a particularly stable chelate ring in silver(I) complexes of unsaturated sulphur and selenium ligands.[3,7] Chelate formation overwhelms the normal inductive effects

TABLE 2

Protonation and complex formation constants of substituted pyridines, RC_5H_4N, at 25 °C and $I = 0{\cdot}10$M (KNO_3) (standard deviations, σ, are given in parentheses)

	log β								
R	HL^+	H_2L^{2+}	$[AgL]^+$	$[AgL_2]^+$	$[CuL]^{2+}$	$[NiL]^{2+}$	$[ZnL]^{2+}$	$[CoL]^{2+}$	$[CdL]^{2+}$
H	5·217(1)		1·95(1)	3·97(1)	2·58(1)	2·08(2)	1·10(1)	1·20(1)	1·35(1)
2-H_2C:CH	5·025(1)		1·75(1)	3·55(1)	1·1(1)	1·2(1)	0·9(1)	0·8(3)	1·1(2)
2-H_2C:CH·CH_2	5·336(2)		2·97(1)	4·8(1)	1·8(1)	1·7(1)	1·6(1)	1·5(1)	1·3(1)
2-H_2C:CH·CH_2·CH_2	5·882(2)		2·72(1)	4·5(1)	2·10(3)	1·7(1)	1·4(1)	1·2(1)	1·3(1)
2-H_2C:CH·CH_2·CH_2·CH_2	5·965(6)		2·27(1)	4·37(1)	2·0(1)	1·6(1)	1·5(1)	1·2(1)	1·0(1)
2-Pr^n	6·116(1)		2·15(3)	4·45(5)	2·2(1)	1·6(1)	1·3(1)	1·4(1)	1·1(1)
2-Me·CH(OH)·CH_2	5·479(3)				2·25(2)	1·7(1)	1·45(5)	1·55(2)	1·6(1)
2-Ph·CH(OH)·CH_2	5·197(1)				2·10(5)	1·65(5)	1·2(1)	1·40(2)	1·35(5)
2-HO·OC·HC:CH	4·559(2)	2·829(2)	1·83(2)	3·6(1)	1·0(1)				
2-(2-py·HC:CH)	4·951(2)	2·811(3)			1·0(2)				
4-H_2C:CH	5·396(4)		1·98(2)	4·08(5)	2·73(1)	2·09(1)	1·6(1)	1·6(1)	1·6(1)
4-(4-py·HC:CH)	5·646(2)	4·411(2)							

[6] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

[7] D. S. Barnes, G. J. Ford, L. D. Pettit, and C. Sherrington, *J. Chem. Soc.* (*A*), 1971, 2883.

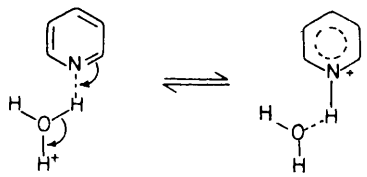
which are apparent when complexes of py and 2-propylpyridine are compared. For example the propyl group increases log β_1 by only 0·2 units, while the 2-allyl group causes an increase of more than 1 unit. As the size of the chelate ring increased from five and one half membered, the stabilisation decreased in a way comparable to that found with sulphur and selenium. Taking 2-propylpyridine as a ligand with comparable inductive effects, the stabilisations in terms of Δ log β_1 values are five and one half membered ring, 0·82; six and one half membered ring, 0·57; and seven and one half membered ring, 0·12. These stabilisations are comparable to those found for ligands containing sulphur and selenium in place of nitrogen, and demonstrate the stability of silver(I) when it is co-ordinated to soft ligands in what could be described, conventionally, as the sp^3 hybridised state rather than the *sp* state normally found with hard donor centres (including py itself).

The influence of chelation and change in stereochemistry is also apparent when the stepwise constants are compared, *i.e.* the quantities log (K_1/K_2). Ligands which are unable to chelate to silver tend to show larger values for K_2 than K_1 [*i.e.* log (K_1/K_2) is negative]. This is contrary to normal statistical arguments and is generally interpreted in terms of changes in stereochemistry of the silver ion when solvation water is replaced by other ligands, particularly those with nitrogen-donor centres. Values of log (K_1/K_2) for the 2-substituted ligands with silver(I) are as follows.

Substituent	log (K_1/K_2)
H	−0·07
$H_2C{:}CH$	−0·05
$H_2C{:}CH{\cdot}CH_2$	+1·2
2-$H_2C{:}CH{\cdot}CH_2{\cdot}CH_2$	*ca.* +1
2-$H_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	+0·17
2-Pr^n	−0·15
4-$H_2C{:}CH$	−0·12

These show clearly that, when chelation is marked, the tendency to co-ordinate a second ligand drops dramatically. Two explanations can be offered for this drop: (*i*) the bis complex regains linear geometry and, in doing so, displaces the olefin group from the co-ordination sphere so causing a drop in stability; or (*ii*) the complex retains an approximately tetrahedral symmetry with both ligands bidentate and therefore $K_2 < K_1$ through statistical and steric factors. The second explanation is favoured since the value of log β_2 for the chelating ligands, particularly (L; R = $H_2C{:}CH{\cdot}CH_2$) is considerably larger than for the non-chelating propyl-analogue. The electronic effect of unco-ordinated olefinic bonds would be expected to encourage a lower stability rather than the higher stability found.

Bivalent Metal-ion Complexes.—All complexes with the bivalent transition-metal ions studied were, as expected, weak. Hence the results have a comparatively low precision. Under the experimental conditions used, bis complexes did not form in measurable concentrations. As a general conclusion, the stabilities followed the order found for protonation, providing no evidence of chelation through



the olefinic bonds. Complexes with substituted pyridines tended to be slightly weaker than those with py itself, suggesting increased steric hindrance when metal ions replace the hydrogen ion. This is reasonable if the hydrogen ion does not have to approach the pyridine nitrogen atom directly but protonates *via* a Grotthus-type mechanism. The stability order for different transition-metal ions with a particular ligand was in general agreement with the Irving–Williams order.

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