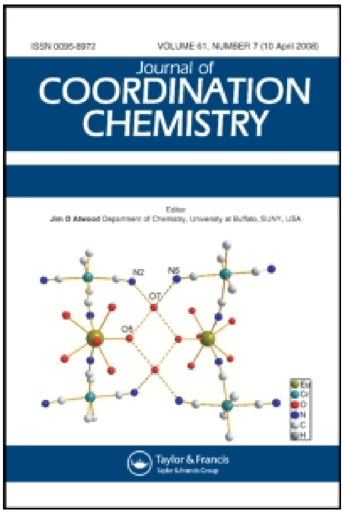

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FIVE CO-ORDINATE 2-METHYLPYRIDINE ADDUCTS OF BIS(SALICYLIDENEIMINATO)NICKEL(II) COMPLEXES

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FIVE CO-ORDINATE 2-METHYLPYRIDINE ADDUCTS OF BIS(SALICYLIDENEIMINATO)NICKEL(II) COMPLEXES

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The interaction of 2-methylpyridine with nickel(II) complexes of a range of substituted salicylideneimines has been investigated. In each case 1:1 base adducts are produced but these are formed incompletely even when 2-methylpyridine is employed as solvent. The five co-ordinate base adducts as paramagnetic and, by combination of solution magnetic and spectral results, the respective formation constants have been calculated. Steric factors appear to be important in the promotion of five co-ordination in these complexes.

INTRODUCTION

The interaction of heterocyclic bases such as pyridine with diamagnetic nickel(II) complexes of substituted salicylideneimines has been studied in considerable detail.[1–6] Most reactions of this type lead to the formation of paramagnetic octahedral adducts containing two molecules of base co-ordinated in the axial sites. Recent evidence demonstrates that formation of such compounds is a stepwise process[7,8] and an investigation of the thermodynamics of formation of selected adducts has enabled calculation of the corresponding stepwise formation constants.[9] We have previously observed[9] that the behaviour of certain nickel complexes of substituted salicylideneimines with pyridine does not parallel their behaviour with 2-methylpyridine which yields only five co-ordinate monoadducts. This tendency for 2-methylpyridine to yield 1:1 adducts with the above complexes is qualitatively similar to its behaviour towards a number of other square-planar nickel complexes containing sulphur-donor ligands.[10–13]

In an endeavour to obtain more definitive information about the formation of such five co-ordinate complexes, we have undertaken a study of the interaction of 2-methylpyridine with the nickel complexes of a range of related substituted salicylideneimines.

EXPERIMENTAL

Preparation of Square Planar Complexes

These were all prepared by reaction of bis(salicylaldehydo)-nickel(II) in methanol with the appropriate amine. All products were recrystallised before use. The complexes, $X = Cl$, $R = C_2H_5$, $i - C_4H_9$, were insufficiently soluble in benzene to be used in this work.

Physical Measurements

All solvents were dried and fractionated before use.

Solution spectra were determined on a Hitachi EPS-3T recording spectrophotometer. The cell was thermostated to 25 ± 0.5°.

Solution magnetic studies were performed on a modified Newport magnetic balance which has been described previously.[9] Measurements were at 25 ± 1°.

Analyses

Carbon, hydrogen and nitrogen analyses were carried out by Dr. E. Challen and Mr. J. Susman of The University of New South Wales. Nickel was determined gravimetrically as the dimethylglyoxime.

RESULTS AND DISCUSSION

Each of the complexes of type (I) shows a single broad absorption in benzene (Table I) which is

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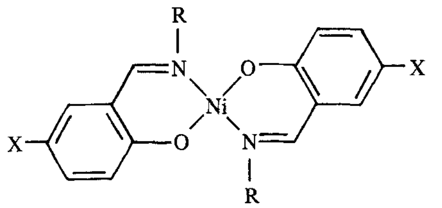
TABLE I

Analytical and spectral data for the square planar bis(salicyclideneiminato)nickel(II) complexes

Complex	Formula		Analyses				Visible spectra[a,b]
			C	H	N	Ni	
$R = C_2H_5, X = H$	$C_{18}H_{20}N_2ONi$	Calcd.	60.90	5.68	7.89	16.5	
		Found	60.63	5.77	7.67	16.3	621 (79)
$R = n\text{-}C_3H_7, X = H$	$C_{20}H_{24}N_2O_2Ni$	Calcd.	62.70	6.32	7.31	15.3	
		Found	62.94	6.46	7.39	15.2	625 (79)
$R = n\text{-}C_4H_9, X = H$	$C_{22}H_{28}N_2O_2Ni$	Calcd.	64.29	6.86	6.81	14.3	
		Found	64.25	6.81	6.78	14.3	621 (80)
$R = i\text{-}C_4H_9, X = H$	$C_{22}H_{28}N_2O_2Ni$	Calcd.	64.29	6.86	6.81	14.3	
		Found	64.68	6.95	6.93	14.4	625 (79)
$R = n\text{-}C_3H_7, X = Cl$	$C_{20}H_{22}N_2O_2Cl_2Ni$	Calcd.	53.15	4.91	6.20	13.0	
		Found	53.08	5.01	6.12	12.9	627 (91)
$R = n\text{-}C_4H_9, X = Cl$	$C_{22}H_{26}N_2O_2ClNi$	Calcd.	55.05	5.46	5.84	12.2	
		Found	55.34	5.34	5.85	12.2	626 (101)

[a] In benzene, concentration 0.0313 M.

[b] In nanometers, molar extinction coefficients in parentheses.

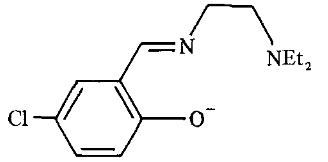


when $X = H$, $R = C_2H_5$, n-C_3H_7, n-C_4H_9 or i-C_4H_9.

when $X = Cl$; $R =$ n-C_3H_7 or n-C_4H_9.

(I)

typical of a square-planar species. However if these compounds are titrated with 2-methylpyridine the rise of new absorptions in both the visible and near-infrared regions are observed. The spectrophotometric titration curves for (I; $X = Cl$, $R = n-C_4H_9$) in the near infrared region are illustrated in Figure 1. From the changes in the visible portion of the spectrum it is apparent for this complex (and indeed for all the complexes of type I) that even in pure 2-methylpyridine there is still evidence for the presence of some square-planar species. However the new absorptions are consistent with the additional presence of paramagnetic five co-ordinate species.[13-15] In particular, the absorption at ~1500 nm is characteristic of a high-spin square pyramidal complex[14] and this absorption can be assigned to the $^3B_1 \rightarrow {}^3E$ transition (C_{4v} symmetry). The spectra are generally similar to those found for the bis-ligand complex of (II)[14] which has been shown by an x-ray structure determination to be square pyramidal (the $-NEt_2$ group of one ligand is uncoordinated).[16,17] This complex has the same combination of donor atoms as the complexes under discussion. It is perhaps significant that in non-polar solvents the complex of (II) exists as an equilibrium mixture of four co-ordinate species (singlet ground state) and five and six co-ordinate species (triplet ground states).[14]



(II)

As suggested by their spectra, it was found that the complexes of type (I) do not exhibit full paramagnetism even in pure 2-methylpyridine. The percentage paramagnetism for each complex is listed in Table II. It is apparent that the degree of paramagnetism of a particular complex depends much more on the presence or absence of a chloro group in the five position of aromatic backbone of the ligand than on a change of alkyl substituent on the imine nitrogen. Since there is no evidence (see below) for the presence of a significant concentration of any other paramagnetic species, the percentage paramagnetism also corresponds to the percentage of five co-ordinate complex in the solution.

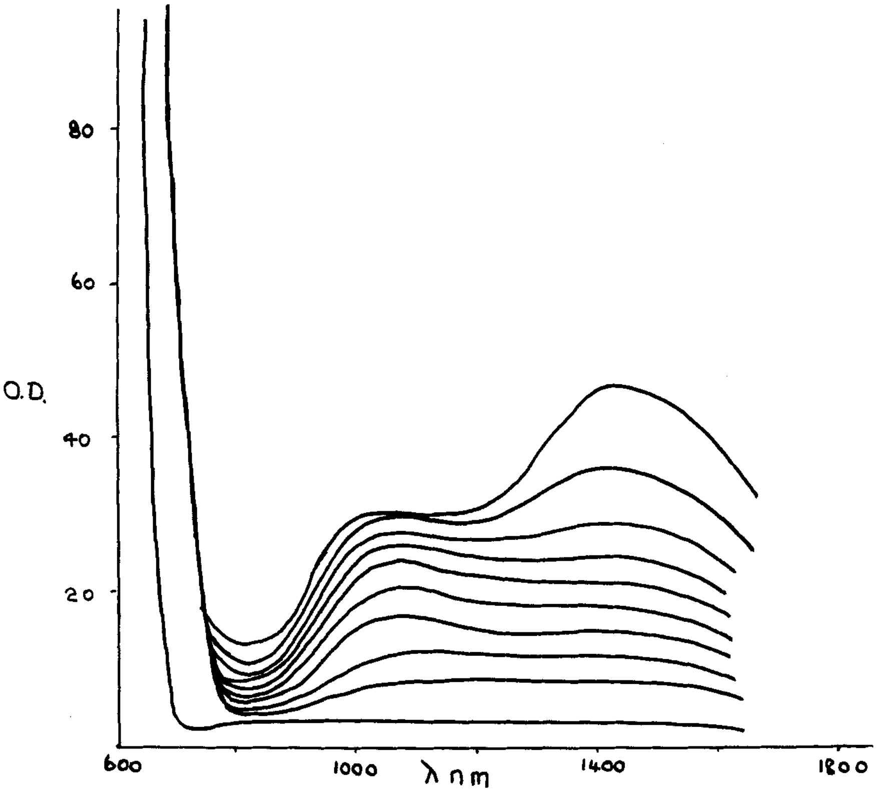


FIGURE 1 The spectrophotometric titration of (I; R = Bu, X = Cl) in benzene (0.031M) with 2-methylpyridine. In order of increasing ϵ values the 2-methylpyridine concentrations are: 0; 0.1458M; 0.3166M; 0.6187M; 0.9505M; 1.3270M; 1.7430M; 3.5070M; 5.1070M; pure 2-methylpyridine.

TABLE II
Magnetic, spectral and formation constant data for the complexes[a]

Square-planar complex	% Paramagnetism[b,c]	Spectral data[b,e]	K for mono-adduct[d] (moles^{-1} l)
I, R = C_2H_5, X = H	29	623(79), 1040(1.9), 1490(6.1)	0.049 ± 0.005[f](0.05)[g]
I, R = n–C_3H_7, X = H	25	623(73), 1030(2.2), 1480(5.7)	0.033 ± 0.003 (0.02)
I, R = n–C_4H_9, X = H	20	621(68), 1021(2.1), 1460(5.6)	0.027 ± 0.003 (0.02)
I, R = i–C_4H_9, X = H	22	625(70), 1060(1.6), 1500(4.0)	0.027 ± 0.002 (0.02)
I, R = n–C_3H_7, X = Cl	55	629(66), 1070(6.4), 1470(16.2)	0.15 ± 0.02 (0.2)
I, R = n–C_4H_9, X = Cl	57	625(47), 1060(8.5), 1460(14.9)	0.18 ± 0.02 (0.3)

[a] Concentration 0.0313 M, temperature 25°.

[b] Square-planar complex in 2-methylpyridine.

[c] Based on a magnetic moment of 3.1 B.M. for complete paramagnetism.

[d] In benzene (25°).

[e] All spectra also show evidence of a weak shoulder at ~860 nm.

[f] Standard deviation for six values of K. From consideration of the likely errors in each of the concentrations used to calculate the K values it seems likely that the actual errors in the K values are of the order of ±0.003 for the first four compounds and ±0.06 for the last two compounds.

[g] Alternate determination solely from spectra data – see text.

From the observed extinction in pure 2-methylpyridine of the band at ~1500 nm coupled with the percentage adduct formation in this solvent, the true molar extinction coefficient for each five co-ordinate complex can be obtained. Using this, the concentration of the five co-ordinate species can be monitored throughout the titration of the corresponding square-planar complexes with 2-methylpyridine. Using the data so obtained, the stoichiometry of each reaction was confirmed by plotting the logarithm of the ratio of the concentrations of complexed and uncomplexed species against the logarithm of the equilibrium 2-methylpyridine concentration (given by $(\text{2-Mepy})_{\text{total}} - (\text{2-Mepy})_{\text{complexed}}$).[18,19] In each case the slope of the line was not significantly different to one. The slope gives the number of ligands adding to form the product and the reactions are thus all of the type: $\text{NiL}_2 + \text{2-Mepy} \rightarrow \text{NiL}_2(\text{2-Mepy})$.

Once the molar extinction coefficients for the five co-ordinate adducts are known, the respective formation constants can also be calculated. Six determinations of each constant were obtained at intervals along the corresponding titration curve and the results meaned (Table II). The individual values so obtained show little variation as the concentration of 2-methylpyridine is altered and this provides additional confirmation that the stoichiometry chosen for the reaction is correct. It has been reported previously that many square-planar nickel salicylideneimines show a slight but varying tendency towards association in solvents such as benzene.[20,21] Thus the values calculated for the formation constants based on the early sections of the titration curves may be less reliable because of possible interference from these other less-defined equilibria. Accordingly no calculations were attempted in that portion of a curve which corresponded to less than ten percent of the total amount of 2-methylpyridine added during the titration.

The small K values imply that the equilibria strongly favour the formation of the four co-ordinate species and under these conditions it is possible to use the equation below[22] to obtain an alternative evaluation of the various K values. The equation is:

$$\frac{1}{X} = \frac{1}{KA(B)} + \frac{1}{A}$$

where (B) is the equilibrium 2-methylpyridine concentration and X and A are defined as $\epsilon_m - \epsilon_u$ and $\epsilon_c - \epsilon_u$, respectively, where ϵ_m is the extinction value of an equilibrium mixture at some given total NiL_2 concentration and ϵ_u and ϵ_c are the extinction values which the total NiL_2 would exhibit if adduct formation were zero or complete, respectively. A plot of $1/X$ against $1/B$ will yield a straight line from which the equilibrium constant may be calculated by determining the slope and intercept. For the case where K is small as an approximation one can substitute the total 2-methylpyridine added for B. This approximation was made in the present calculations which are also based on the absorption at ~1500 nm in the near infrared spectrum. This procedure provides an alternative means of obtaining confirmatory values for the formation constants which are independent of the magnetic data required in the previous method. It is however subject to greater error. The values obtained by this procedure are listed in Table II and, in general, show quite good agreement with those obtained previously.

It is apparent from Table II that the complexes containing the five-chloro-substituted ligands yield more stable adducts than their unsubstituted analogues. The variation of the alkyl substituent on the imine nitrogen is also seen to coincide with small but progressive changes in the respective K values. However it is inappropriate to ascribe these small differences to specific steric or electronic effects. For this to be a possibility it is first necessary to know the magnitude of the enthalpy and entropy changes associated with adduct formation. For the present system it is not possible to obtain a satisfactory measure of ΔH° values by calorimetric methods because of experimental problems associated with the relatively high heat of solution of 2-methylpyridine in benzene coupled with the small K values for adduct formation.[23] Similarly, determination of ΔH° values indirectly from a plot of log K versus reciprocal temperatures is not satisfactory because of errors inherent in the procedure when K is small.[23,24]

It is pertinent to consider why 2-methylpryidine yields only 1:1 adducts with these square-planar species whereas generally nickel(II) complexes of this type yield bis-base adducts with a range of other heterocyclic bases such as pyridine and 4-methylpyridine.[9] Square-planar complexes of certain sulphur-donor ligands have also been reported to yield mono- and bis-adducts with 2-methylpyridine and pyridine, respectively.[11-13] For example, even in pure 2-methylpyridine, the square planar nickel-complexes of a range of substituted dithiophosphato ligands yield only mono-base adducts. Their behaviour thus parallels the behaviour of the present complexes in this solvent. The reluctance of 2-methylpyridine to yield bis-base adducts has been ascribed to steric hindrance[13] although, for the present complexes, the nature of such hindrance remains unexplained. On first consideration, it is difficult to see how attachment of a 2-methylpyridine molecule in one axial position of a planar metal–ligand system could sterically inhibit attachment of a second base molecule at the other axial site (*trans* to the first). Nevertheless Orioli[25] points out in a recent review that, although many such five co-ordinate nickel(II) complexes are known, this geometry must still be considered unusual and is favoured by the use of bulky ligands which sterically prevent six co-ordination. A steric constraint on six co-ordination thus seems likely for the present complexes and, with regard to this, the observation that complexes of type (**I**) are not completely flat is very likely significant.[8,26,27] Such complexes are capable of existing in two isomeric forms in both of which the aromatic rings are inclined at an angle to the plane containing the four donor atoms and the metal ion. One such isomer contains both aromatic rings on the same side of this plane whereas they are inclined on opposite sides in the second isomer. In the absence of added base it would be expected that the second of these isomers would be preferred and an x-ray structure determination[27] of (**I**; R = Et, X = H) has shown that this complex does in fact exist in the solid in the second isomeric form with the aromatic rings each subtending an angle of ~23° to the plane containing the donor atoms. In addition, for (**I**; R = 2,6-$Et_2C_6H_3$–, X = H), two well characterised dimorphic forms have been isolated[8] and these have been suggested to be isomers of the type just discussed.

As already mentioned, it appears that steric factors are the cause of the different behaviour of pyridine and 2-methylpyridine towards complexes of type (**I**). Co-ordination of one molecule of 2-methylpyridine could be expected to promote formation of the conformer in which both aromatic rings are on the side of the molecule away from the co-ordinated base. Molecular models indicate that, if this occurs, the co-ordination of a second bulky 2-methylpyridine in the sixth (octahedral) site will be hindered and hence formation of a five co-ordinate adduct promoted. Nevertheless attempts to isolate the solid adducts by crystallisation of the corresponding square-planar complexes from 2-methylpyridine were all unsuccessful and resulted instead in the recovery of the respective square-planar complexes.

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