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The Interaction of Heterocyclic Bases with Square-Planar Nickel(II) Complexes of Substituted Salicylaldimines

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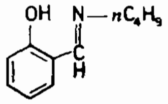
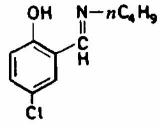
Received November 24, 1972

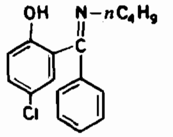
The interaction of pyridine and 4-methylpyridine with the square-planar nickel complexes of three salicylaldimine type ligands has been investigated. Spectroscopic studies indicate that the bases add in a stepwise manner such that five-coordinate intermediates are produced; however in each case the final product is six-coordinate. In contrast, addition of excess 2-methylpyridine yields only the corresponding mono-base adducts. Combination of solution magnetic susceptibility studies with the spectroscopic data has led to estimation of stepwise stability constants. For each compound $K_2 > K_1$. Thermometric titrations have also been performed and have enabled calculation of the corresponding ΔH^0 and ΔS^0 values. Attempts to isolate the five-coordinate species have not been successful but a range of bis-base adducts has been isolated and characterised.

Introduction

The chemistry of bis-ligand nickel(II) complexes of a large number of substituted salicylaldiminato ligands has been studied fairly intensively.[2-4] Many such complexes are known to react with heterocyclic bases to form paramagnetic adduct species. Although the formation of octahedral species containing two coordinated base molecules has been recognised for a considerable time,[5-9] it is only recently that evidence has been presented for the formation of mono-base adducts. Such five-coordinate complexes have been observed for only a very restricted number of salicylaldimine-ligand types.[10,11] The present study was initiated to investigate whether five-cordinate species might occur more generally for this type of complex than so far demonstrated. The complexes of three salicylaldimines containing considerably different substitution patterns (I-III) were chosen and their interaction with heterocyclic bases studied. Independent spectroscopic, magnetic, and calorimetric studies in benzene have been used to gain information about the respective equilibrium systems.


I N-*n*-butylsalicylaldimine


II N-*n*-butyl-5-chlorosalicylaldimine


III N-*n*-butyl-5-chloro-2-hydroxybenzophenoneimine

Experimental Section

Preparations. *NiL_2 (LH = ligands I and II)* were prepared by reaction of bis(salicylaldehydo)nickel(II) in alcohol directly with the appropriate amine.[2] The Schiff base complexes which formed were recrystallised before use.

NiL_2 (LH = ligand III). To nickel acetate (0.1 mole) dissolved in boiling methanol (100 ml) was added the Schiff base (0.2 mole) dissolved in methanol (50 ml). On the addition of piperidine (1 ml) the complex precipitated. The product was filtered off, washed with boiling methanol, and dried at room temperature.

Base Adducts (NiL_2Base_2). Complexes of the type NiL_2 were dissolved in hot base. The solution was filtered then allowed to evaporate slowly at room temperature until crystals of the adduct formed. These

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(1) (*a*) *University of New South Wales*; (*b*) *James Cook University of North Queensland, to whom correspondence should be addressed*; (c) *Wollongong University College.*

(2) R.H. Holm, G.M. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, *7*, 83 (1966).

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Table I. Analytical data[a] for complexes of thc type ML_2 and ML_2 $base_2$.

Ligand	Base	Formula	C	H	N	Ni
I	—	$C_{22}H_{28}N_2O_2Ni$	64.29	6.86	6.81	14.3
			64.25	6.81	6.78	14.3
I	Pyridine	$C_{32}H_{38}N_4O_2Ni$	67.52	6.73	9.84	10.3
			68.10	6.87	9.41	10.2
I	4-Methylpyridine	$C_{34}H_{42}N_4O_2Ni$	68.35	7.08	9.38	9.8
			68.69	7.14	9.34	9.8
II	—	$C_{22}H_{26}N_2O_2Cl_2Ni$	55.05	5.46	5.84	12.2
			55.34	5.34	5.85	12.2
II	Pyridine	$C_{32}H_{36}N_4O_2Cl_2Ni$	60.23	5.69	8.78	9.2
			60.30	5.60	8.44	9.2
II	4-Methylpyridine	$C_{34}H_{40}N_4O_2Cl_2Ni$	61.27	6.05	8.41	8.8
			61.72	6.00	8.36	8.6
III	—	$C_{34}H_{34}N_2O_2Cl_2Ni$	64.60	5.42	4.43	9.3
			65.02	5.43	4.39	9.2
III	Pyridine	$C_{44}H_{44}N_4O_2Cl_2Ni$	66.85	5.61	7.09	7.4
			67.11	5.63	7.22	7.4
III	4-Methylpyridine	$C_{46}H_{48}N_4O_2Cl_2Ni$	67.48	5.91	6.84	7.2
			67.48	5.86	6.51	7.2

[a] Percent calculated data are in the first row and percent found in the second row for each compound.

were filtered off, washed with 40-60° petroleum ether, and dried at room temperature.

Magnetic Moments. Both solution and solid moments were determined by the Gouy method. The solution moments were determined on a modified Newport single-temperature magnetic balance. The sample was held in a 8 mm diameter sample tube which was calibrated using nickel chloride solution. The 1½ inch electromagnet (type C) in conjunction with a Newport power supply (type VR3) was fed from a stabilised mains supply. The magnet was cooled with water at 10° and produced a field of ~8000 Oe. To ensure adequate temperature equilibration the sample tube and magnet were totally enclosed in a draught cover. The magnet was mounted on tracks so that it could be positioned from outside the draught cover by using a remote control lever. All measurements were taken after an equilibration time of at least one hour. The temperature of measurement was 25° ± 1°. All solution measurements were carried out in benzene at a concentration of 0.0313 *M*. The need for moderately soluble complexes influenced the selection of N-*n*-butyl ligand derivatives as these tend to yield more soluble complexes than similar ligands containing shorter chain alkyl substituents.

Visible-Near Infrared Spectra. Solid state spectra were obtained on a Zeiss PMQ II spectrophotometer with an RA3 reflectance attachment. Solution spectra were obtained on a Hitachi EPS-3T recording spectrophotometer.

Calorimetric Measurements. These were performed at 25° using a LKB 8700 precision calorimeter. Details of the technique used, including treatment of solvents, have been described previously.[12]

Thermogravimetric Measurement. This gas determined by Dr. P.S.K. Chia (University of New South Wales) on a Stanton thermobalance, model TR-O1.

Analyses. Carbon, hydrogen and nitrogen analyses were carried out by Dr. E. Challen and Mr. J. Susman of the University of New South Walles. Nickel was determined gravimetrically as the dimethylglyoxime after the complexes had been decomposed in a mixture of concentrated nitric acid, sulphuric acid and perchloric acid. The analytical data are summarised in Table I.

Results and Discussion

Spectrophotometric studies of the nickel(II) complexes of the ligands (I-III) dissolved in pyridine indicate that for each complex the original square planar species is converted completely to the corresponding bis-pyridine adduct. As noted previously for the complex of I,[9] the spectra (Table II) are best interpreted using a pseudo octahedral model in which two pyridine molecules occupy *trans* positions. The $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions are observed at about 1000 nm and 600 nm, respectively. Magnetic moment determinations on the pyridine solutions confirm that full paramagnetism is developed in each case with all compounds showing moments in the typical range 3.1-3.2 BM (Table III). Analogous spectral and magnetic behaviour was observed when 4-methylpyridine was substituted for pyridine.

If each of the square planar species in benzene is titrated with pyridine then the corresponding spectra show an initial rise then fall of a distinctive band in the near infrared region (at about 1500 nm). Similar behaviour was observed when 4-methylpyridine was used as the titrant except that this led to a more abundant formation of the intermediate at lower base concentrations. Figure 1 illustrates the spectra from one such titration.

Use of 2-methylpyridine as titrant does not lead to formation of octahedral bis-base adducts but for each case the species absorbing at ~1500 nm is the only one produced even in pure base. Figure 2 illustrates the spectrum of the nickel complex of II in pure 2-methylpyridine.

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Table II. Visible and near IR electronic spectra[a] of Nickel complexes of the type NiL_2 and NiL_2Base_2.

Ligand	Base	Solid State	Solution[b] Benzene	Solution[b] Pyridine	Solution[b] 4-Methyl Pyridine	Solution[b] 2-Methyl Pyridine
I		610	621(80)	586(12.1) 995(13.5)	586(12.0) 990(14.0)	621(68) 1040(2.0) 1470(6.1)
I	Pyridine	595 960				
I	4-Methylpyridine	560 950				
II	—	595	626(101)	586(13) 990(13.9)	595(15.9) 995(14)	625(47) 1060(8.5) 1460(14.9)
II	Pyridine	600 970				
II	4-Methylpyridine	600 990				
III	—	595	582(149)	594(15.4) 1015(15)	585(12.8) 1015(15)	580(140) 1020(2.4) 1560(4.4)
III	Pyridine	595 990				
III	4-Methylpyridine	590 980				

[a] in nanometers, ε values in parentheses. [b] Solution spectra at concentration 0.0313 molar.

Table III. Magnetic moments[a] of octahedral complexes in the solid and solution[b].

Ligand	$NiL_2(pyridine)_2$ Solid	$NiL_2(pyridine)_2$ Solution	$NiL_2(4\text{-methylpyridine})_2$ Solid	$NiL_2(4\text{-methylpyridine})_2$ Solution
I	3.15	3.18[c]	3.19	3.14
II	3.02	3.21	3.22	3.06
III	3.09	3.11	3.15	—[d]

[a] μ_{eff} in B.M. (298°K); [b] solution in pure base (concentration 0.0313 M); [c] Reported previously 3.15B.M.[9], 3.14B.M.[13]; [d] Precipitates from solution during measurement.

The near infrared spectra observed for all of these complexes in base are consistent with the formation of paramagnetic five-coordinate complexes. The bisligand nickel complex of IV has very similar low extinction absorptions in the near infrared region[14,15] and an x-ray structure determination has shown it to have a square pyramidal geometry V.[16,17] This complex is high spin and contains the same combination of donor atoms as in the complexes under discussion. By analogy with the spectrum of V, the

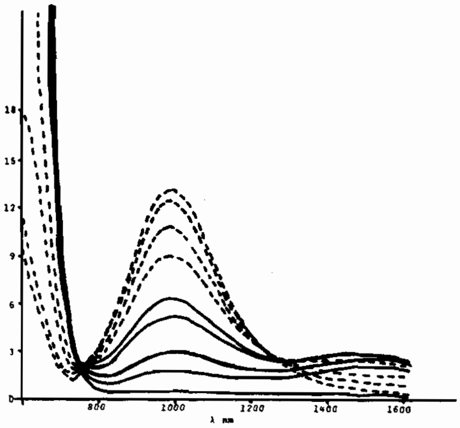

Figure 1. Spectrophotometric titration of bis(N-*n*-butylsalicylialdiminato)nickel(II) in benzene with 4-methylpyridine. In order of increasing ε values (at 1000 nm) the molar base concentrations are: 0; 2.427×10^{-2}; 4.102×10^{-2}; 7.217×10^{-2}; 9.257×10^{-2} 14.35×10^{-2}; 21.26×10^{-2}; 49.57×10^{-2}; 1009×10^{-2} (pure 4-methylpyridine).

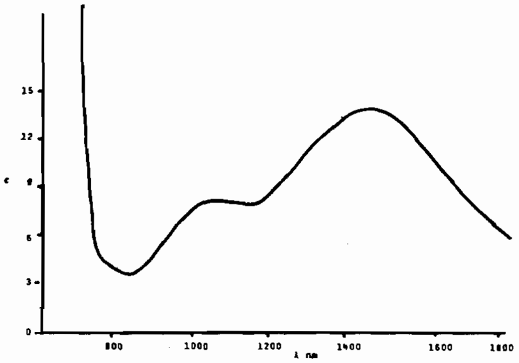

Figure 2. Absorption spectrum of bis(N-*n*-butyl-5-chlorosalicylaldiminato)nickel(II) in 2-methylpyridine.

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(13) L. Sacconi, P. Padletti and G. Del Re, *J. Amer. Chem. Soc.*, *79*, 4062 (1957).

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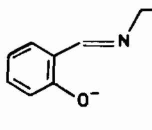
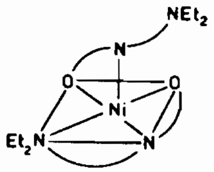
(17) P.L. Orioli, M. Di Vaira, and L. Sacconi, *J. Amer. Chem. Soc.*, *88*, 4385 (1966).



IV



V

absorption at ~1500 nm (Figure 1 and Table II) for each complex in the presence of base can be tentatively assigned to the $^3B_1 \rightarrow {}^3E$ transition (assuming C_{4v} microsymmetry). A number of other complexes which are considered to be square-pyramidal also show similar near infrared spectra.[18,19] The visible-region spectra of the complexes is of little diagnostic value since in this region any four (or six) coordinate species in equilibrium with the five-coordinate species will also give rise to overlapping absorptions.

It thus appears that pyridine and 4-methylpyridine react with the square planar complexes in a stepwise manner:

$$ML_2 + base \rightleftharpoons ML_2base$$
$$ML_2base + base \rightleftharpoons ML_2base_2.$$

La Mar[10] has previously postulated, from NMR contact shift evidence, that in chloroform the complex of I reacts with pyridine in this manner. With 2-methylpyridine it is apparent that only the first of the above steps occurs and indeed magnetic susceptibility measurements on all three complexes in 2-methylpyridine indicate that in no case is the nickel completely present in the paramagnetic (five coordinate) form. The percentage paramagnetism (based on the respective values in pyridine) was found to be nineteen percent for the complex of I, fifty-three percent for the complex of II, and nineteen percent for the complex of III. Thus even in the presence of pure 2-methylpyridine only partial formation of the respective mono-base adducts occurs.

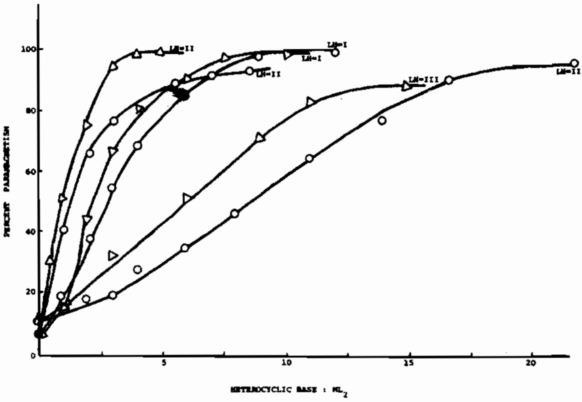


Figure 3. Magnetic titration curves for complexes of the type NiL_2 in benzene with pyridine (O) and 4-methylpyridine (Δ).

Magnetic titrations have been performed during which the rise of paramagnetism was followed as each of the square planar species was titrated with pyridine or 4-methylpyridine. The results of these titrations are shown in Figure 3. For the square-planar complex of any particular ligand the curves illustrate clearly that the interaction with 4-methylpyridine leads to formation of more stable adducts than those formed with pyridine. The stabilities thus parallel the pK_b values for the heterocyclic bases. In addition it is obvious from the curves that for a given base the order of stabilities of the complexes depends markedly on the substitution pattern of the bidentate salicylaldimine involved. Previous studies[20,21] suggest that substitution of a phenyl group for the imine hydrogen of I would reduce the tendency for the nickel complex to form base adducts whereas substitution of a chloro group in position five of the aromatic ring of I should have the reverse effect. The behaviour of the present compounds is in accord with these observations.

Combination of the spectral titration data with the magnetic titration data can be used to obtain an estimate of stepwise stability (concentration) constants for the addition of base to the respective square planar species. For example, consider the reaction of pyridine with one of the bis-ligand nickel complexes:

$$K_1 = \frac{[ML_2Py]}{[ML_2][Py]}; \qquad K_2 = \frac{[ML_2Py_2]}{[ML_2Py][Py]}.$$

From the percent paramagnetism of the complex in pure 2-methylpyridine combined with the observed extinction value at 1500 nm, the true molar extinction value for the 2-methylpyridine mono-adduct can be calculated. The concentration of the mono-pyridine adduct at any point along the pyridine titration curve can then be estimated directly from the spectral data if it is assumed that the mono-pyridine and mono-2-methylpyridine adducts both have equal molar extinctions. The percent nickel present in the paramagnetic state can be obtained directly from the magnetic titration curve and from this the molar concentration of square planar complex determined:

$$[ML_2] = \frac{(100-x)}{100}C \qquad \text{where } x = \text{percent paramagnetism}, \quad C = 0.0313M$$

The remaining concentrations are then given by:

$$[Py] = [Py]_{total} - [ML_2Py] - 2[ML_2Py_2]$$

and

$$[ML_2Py_2] = [Ni]_{total} - [ML_2] - [ML_2Py]$$

As observed by other workers[5,22] for this type of compound the bis-ligand complexes are not completely diamagnetic in benzene even in the absence of added base. Nickel(II) salicylaldiminato complexes have been shown to exist in solution as equilibrium mixtures of octahedral polymers, tetrahedral monomers and planar monomers.[2] The predominant spe-

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[19] J.R. Angus, G.M. Woltermann, and J.R. Wasson, *J. Inorg. Nucl. Chem.*, 33, 3957 (1971) and references therein.

[20] D.P. Graddon and G.M. Mockler, *Austral. J. Chem.*, *21*, 617 (1968).

[21] D.P. Graddon and G.M. Mockler, *Austral. J. Chem.*, *21*, 907 (1968).

[22] H.C. Clark, K. Macvicar, and R.J. O'Brien, *Can. J. Chem.*, *40*, 822 (1962).

Table IV. Thermodynamic parameters for the addition of base to NiL_2 complexes[a].

Ligand	Base	K_1[b,c]	K_2[b,c]	K_{12}[b]	$-\Delta G_{12}^\circ$[b] (kJ mol^{-1})	$-\Delta H_{12}^\circ$ (kJ mol^{-1})	$-\Delta S_{12}^\circ$ (JK^{-1} mol^{-1})	K_{12}[d]	$-\Delta G_{12}^\circ$[d] (kJ mol^{-1})
I	pyridine	3.1	91	282±80	14.0±0.8	63±4	164±18	186±30	13.0±0.5
I	4-methylpyridine	5.0	100	500±100	15.4±0.9	56±6	136±23	[e]	[e]
II	pyridine	—	—	~2000	—	68±5	—	1600±200	18.3±0.3
II	4-methylpyridine	—	—	>5000	—	63±3	—	[e]	[e]
III	pyridine	0.6	34	20±10	7.4±1.7	62±5	183±57	15.1±2.0	6.7±0.3
III	4-methylpyridine	1.0	47	47±15	9.5±0.8	44±5	116±23	35±5	8.8±0.4

[a] At 0.0313*M* and 25°. [b] Calculated from spectral and magnetic data. [c] Each value is the mean of six determinations spaced along the magnetic titration curve. The range of values obtained for the complexes of in the above table are:

	Pyridine Case						4-Methylpyridine Case					
paramagnetism(%)	35	44	59	69	78	85	35	40	53	67	76	84
K_1	2.8	2.9	3.0	3.0	3.2	3.7	4.0	4.2	5.1	5.8	5.5	5.6
K_2	102	100	90	90	85	79	100	105	99	103	102	93

[d] Calculated directly from thermometric titration data - see text. [e] Not determined.

cies varies from ligand to ligand and solvent to solvent and is temperature dependent.

The magnetic behaviour in solution of the nickel complex of I has been studied over a range of concentrations and temperatures[5] It was shown that the equilibrium involved is of the planar monomer (diamagnetic) - octahedral polymer (paramagnetic) type. Because of this competing equilibrium at the low-end of the magnetic titration curve, only that portion of each curve above thirty-five percent paramagnetism has been used for stability constant calculations. The upper limit for calculation was chosen as eighty-five percent paramagnetism as above this value the errors involved in determination of the various concentrations increase considerably since they become very dependent on the accuracy of the value taken as representing one hundred percent paramagnetism.

The calculated constants for the complexes of I and III are listed in Table IV. For each complex the value of K_2 is somewhat greater than K_1 indicating a preference of the metal in these systems for six coordination rather than five. The individual values of the constants are not of high accuracy because of the assumptions inherent in the procedure. However we believe that the errors quoted for the various K_{12} values are realistic assessments of the errors involved. They were assessed after consideration of the likely errors in the concentrations of the individual species used in the calculations. As demonstrated in Figure 3, the stabilities of the base adducts of the nickel complex of II are considerably greater than for the complexes of the other two salicylaldimines. For such high stabilities the values, of the constants become very sensitive to the shape of the magnetic titration curves and the method can only be expected to yield semiquantitative results. However it is apparent that both pyridine and 4-methylpyridine yield adducts for which $K_1 \ll K_2$.

Provided $K_1 \ll K_2$ and that ΔH_1° is not large compared to ΔH_2°, the thermometric titration curves can be used for direct estimation of the K_{12} values as described previously.[23] The validity of the above assumptions for the present reactions is confirmed by the excellent agreement of the K_{12} values (Table IV) obtained by this procedure with the values obtained from the magnetic and spectral data.

Thermometric titrations of the three compounds with pyridine and 4-methylpyridine have been performed at 25° and the overall ΔH° values determined for the reaction: $ML_2 + 2B \rightarrow ML_2B_2$. Combination of these values with the magnetic and spectral work enables calculation of the corresponding ΔG° and ΔS° values and these are tabulated in Table IV.

Crystallisation of each of the square-planar diamagnetic complexes from pure base (pyridine or 4-methylpyridine) leads in each case to isolation of the corresponding paramagnetic bis-base adducts. The visible spectra of the solids once again show the expected octahedral transitions at ~950 nm $(^3A_{2g} \rightarrow {}^3T_{2g})$ and at ~600 nm $(^3A_{2g} \rightarrow {}^3T_{1g})$ and all have magnetic moments indicative of triplet ground states.

Attempts to isolate five-coordinate complexes by crystallisation of the square-planar complexes from 2-methylpyridine were unsuccessful and resulted only in the recovery of the diamagnetic starting complexes. These results parallel the behaviour of Bis(O,O'-diisopropyldithiophosphate)nickel(II) which yields bis-adducts from both pyridine and 4-methylpyridine but fails to yield an isolatable adduct from 2-methylpyridine.[24]

A thermogravimetric study of the bis-pyridine adduct of the complex of (II) indicates that both pyridine molecules are removed quantitatively over the temperature range 45°-135° (calculated for loss of two pyridines, 24.8%; found 24.9%). Since the thermogravimetric curve indicates a smooth continuous loss of weight, there is no evidence for the formation of a five coordinate intermediate under these conditions.

Conclusions

Although previous workers have demonstrates that pyridine reacts with the square-planar nickel complexes of certain substituted salicylaldimines in a two-step reaction, no determinations of the corresponding step-

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[23] D.R. Dakternieks and D.P. Graddon, *Austral. J. Chem.*, *24*, 2509 (1971).

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wise stability constants have been made. The present work extends the range of such complexes which have been demonstrated to undergo a stepwise reaction with pyridine and by combination of the results from spectral and magnetic studies, estimates of the respective stability constants have been obtained. The behaviour of 4-methylpyridine with each of the complexes is qualitatively similar to pyridine although the former yields more stable adducts. In contrast to pyridine and 4-methylpyridine, 2-methylpyridine gives only a mono-adduct when reacted with each of the square planar species.

Acknowledgment. D.P. Graddon and L.F. Lindoy acknowledge the Australian Research Grants Committee for financial support of this work.