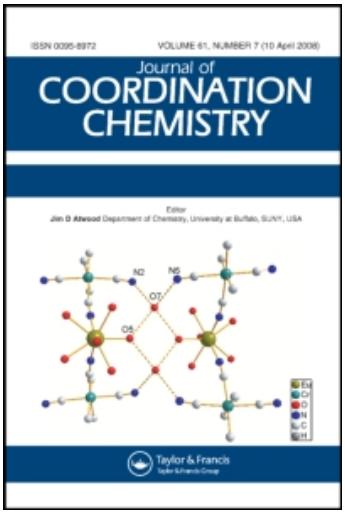

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ADDUCTS OF 1,11-BIS(2'OXOPHENYL)-2,6,10-TRIAZAUNDECA-1,10-DIENATONICKEL(II) WITH PYRIDINE-TYPE BASES

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Adduct formation constants for 1,11-bis(2'-oxophenyl)-2,6,10-triazaundeca-1, 10-dienato-nickel(II), NiSalDPt, with over twenty pyridine-type bases in benzene solution have been determined. An approximately linear relationship between the logarithm of the adduct formation constant and the pK_a values for the pyridine derivatives unsubstituted in the α position, and unexpectedly for 2-aminopyridine and its 3-,4- and 5-methyl derivatives, is obeyed. Contact shifts of ^1H nmr signals in aminopyridines induced by NiSalDPT indicate that all the compounds except 2-amino-6-methylpyridine coordinate *via* the nitrogen atom of the heterocyclic ring. An upfield induced shift of the amine protons signal and unequal shifts of the resonances of carbon bonded protons in the 3 and 5 positions of the latter compound indicate coordination through the primary amine group.

INTRODUCTION

Few years ago Sacconi and Bertini[1] reported the preparation of several five-coordinate nickel(II) complexes with Schiff bases derived from salicylaldehyde and 1,7-diamino-4-azaheptane and their derivatives. In order to check the usefulness of the simplest complex from this series as a reference acid for establishing the relative base strengths of heterocyclic bases in benzene solution we have determined the adduct formation constants for the reaction 1,11-bis(2'-oxophenyl)-2,6,10-triazaundeca-1,10-dienato-nickel(II), NiSalDPT, with several pyridine derivatives in this solvent. Because of the low stability of the adducts as well as different spectral characteristics of reactants and products, the adduct formation constants have been evaluated from spectrophotometric data. To our knowledge only one stability constant for the NiSalDPT-base system has been reported.[1] In order to establish the coordination site in aminopyridines we have also studied shifts of ^1H nmr resonances induced by NiSalDPT.

EXPERIMENTAL

Preparation of Compounds

The nickel complexes 1,11-bis(2'-oxophenyl)-2,6,10-triazaundeca-1,10-dienato-nickel(II), NiSalDPT, and its methyl derivative 1,11-bis(2'-oxophenyl)-6-methyl-2,6,10-triazaundeca-1,10-dienatonickel(II), NiSalMeDPT, were prepared according to the literature method.[1] The products were recrystallized from chloroform-petrol or benzene-cyclohexane mixture to give dark green crystals with m.p. 271° for NiSalDPT (Lit. 271–273°[1]) and 272° for NiSalMeDPT (lit. 270–275°[1]).

The adduct NiSalMeDPT-2-aminopyridine was prepared by adding cyclohexane to the NiSalMeDPT solution in benzene containing an excess of 2-aminopyridine. Anal: Calcd. for $C_{25}H_{29}N_5O_2Ni$: C, 61.93; H, 6.20; N, 13.89%. Found: C, 61.84; H, 6.20; N, 13.85%.

Physical Measurements

The absorption spectra were recorded with Unicam SP 500 and Carl Zeiss Jena VSU-2P instruments equipped with constant temperature cell housings. Benzene was purified by the standard procedure used for spectrophotometric measurements. The bases were otained from Fluka (methyl- and dimethylpyridines), Koch-Light (aminopyridines, methylaminopyridines and 2-methoxypyridine), Loba (2-cyanopyridine), International Enzyme Ltd., (3-cyanopyridine) and Schuchardt (4-cyanopyridine). They were purified until their physical properties agreed closely with values reported in the literature. Usually they were refluxed over potassium hydroxide and fractionated through a Vigreux column, the constant boiling fraction being collected. The solutions of bases and NiSalDPT were prepared by weight.

^{1}H nmr spectra were recorded in deuterated chloroform at 80 MHz with a Tesla BS 487 spectrometer operating at 25°. Hexamethyldisiloxane was employed as an internal reference. NiSalDPT was added incrementally to the base solution to yield mol ratios of 0.05–0.40. Linear graphs were obtained by least-squares fitting of the experimental data. The ir spectrum of the NiSalMeDPT-2-aminopyridine adduct was recorded with a Perkin Elmer 257 spectrometer in a hexachlorobutadiene mull.

Molecular weights were determined in a vapor pressure osmometer (Model 301 A).

RESULTS AND DISCUSSION

Molar weight determination shows that NiSalDPT is monomeric in dilute benzene solution. It reacts with pyridine-type bases to yield 1:1 adducts, their stoichiometry being shown by well defined isosbestic points and the constancy of the equilibrium constant value (*1*)

$$K_{add} = [\text{Adduct}]/[\text{NiSalDPT}][\text{Base}] \qquad (1)$$

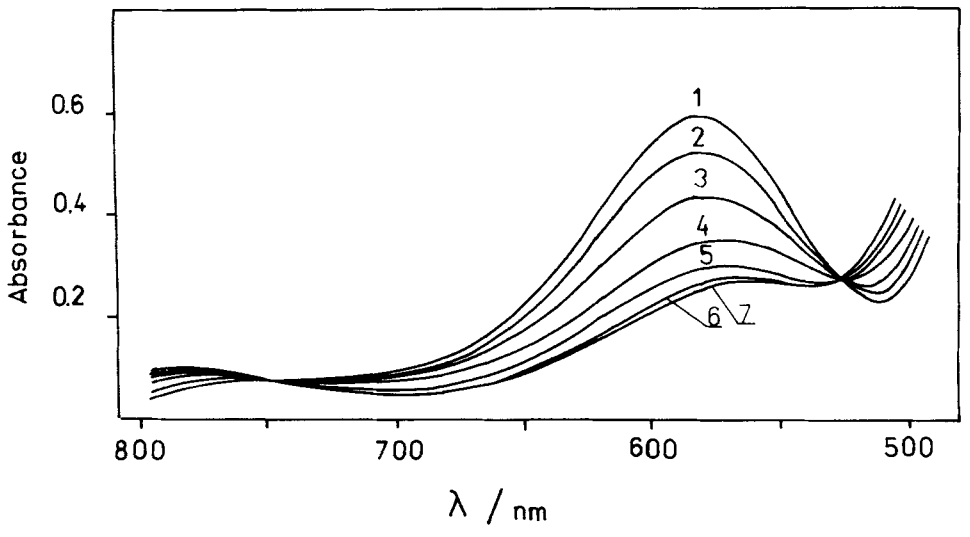

FIGURE 1 Absorption curves for the NiSalDPT — 4-methylpyridine system in benzene solution at 25°; concentration of NiSalDPT 8.43 × 10^{-3}M; concentration of base: 1, 0; 2, 2.65 × 10^{-3}M; 3, 6.80 × 10^{-3}M; 4, 1.15 × 10^{-2}M; 5, 1.61 × 10^{-2}M; 6, 2.04 × 10^{-2}M; 7, 2.57 × 10^{-2}M.

TABLE I
Adduct Formation Constants, K_{add}, in Benzene at 25°

No	Base	pK_a	Ref.	K_{add}	$-\Delta e^a$
1	Pyridine	5.31	7	65.1[1]	
				77.8±3.2	53.4±0.6
2	2-Methoxypyridine	3.28	7	0.52±0.04	50±2
3	2-Methylpyridine	6.03	7	2.17±0.06	43.3±0.8
4	3-Methylpyridine	5.76	7	95.6±5.4	53.4±0.3
5	4-Methylpyridine	6.12	7	134±6	53.8±0.3
6	2,4-Dimethylpyridine	6.74	7	4.4±0.2	46.2±1.2
7	2,5-Dimethylpyridine	6.43	7	2.3±0.1	41.0±1.8
8	2,6-Dimethylpyridine	6.71	7	no complexation	
9	3,4-Dimethylpyridine	6.81	7	119±5	53.0±0.5
10	3,5-Dimethylpyridine	6.23	7	99±13	52.4±0.3
11	2-Cyanopyridine	-0.3	6	8.0±0.8	53.0±0.3
12	3-Cyanopyridine	1.45	6	52.1±2.7	49.0±2.3
13	4-Cyanopyridine	1.90	6	37.5±0.2	52.2±0.5
14	2-Aminopyridine	6.71	7	101±4	56.5±1.4
15	3-Aminopyridine	6.04	7	88.5±1.0	56.5±1.1
16	4-Aminopyridine	9.12	7	221±8	52.9±0.3
17	2-Amino-3-methylpyridine	7.24	6	135±5	53.3±0.7
18	2-Amino-4-methylpyridine	7.48	6	118±5	52.3±0.7
19	2-Amino-5-methylpyridine	7.22	6	165±5	53.1±0.4
20	2-Amino-6-methylpyridine	7.41	6	3.0±0.8	8±2
21	Quinoline	4.89	7	2.6±0.8	33.4±0.3

[a]$\Delta\varepsilon$ is the difference between the absorption coefficients of NiSalDPT-base adduct and free NiSalDPT at 590 nm in benzene solution.

over a wide range of mol ratios of base to nickel complex. A set of absorption curves for the NiSalDPT-4-methylpyridine system is shown in Figure 1.

The adduct formation constants K_{add} have been determined numerically[2] from the absorption data obtained at 590 nm. The calculated values are listed in Table I.

The K_{add} values span the range from 221±8 for 4-aminopyridine to 0 (no complexation) for 2,6-dimethylpyridine. A numerical study of the correlation between log K_{add} values and base strength of donors, expressed as the negative logarithm of the ionisation constants of the conjugated acids in water, has revealed a linear relation of the form (*2*),

$$\log K_{add} = 0.094\ pK_a + 1.45 \qquad (2)$$

for adducts of pyridine, 3-methylpyridine, 4-methylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 3-cyanopyridine, 4-cyanopyridine, 3-aminopyridine, 4-aminopyridine, 2-aminopyridine, 2-amino-3-methylpyridine, 2-amino-4-methyl-pyridine and 2-amino-5-methylpyridine. The linear correlation factor is R = 0.94 (Figure 2). Points lying considerably below the straight line belong to adducts of derivatives comprising the methoxy, methyl and cyano groups in position 2 and indicate a marked steric effect of these substituents. Surprisingly, the points corresponding to K_{add} values of 2-aminopyridine and its 3-, 4- and 5-methyl derivatives fit the line although the amino group is known to exert a steric effect comparable to cyano or methoxy groups; values of Taft's steric parameter E_S are -0.61, -0.55 and -0.51 for the amino, methoxy and cyano groups respectively.[3]

In order to identify the preferential binding sites in aminopyridines we studied ^1H nmr shifts induced by NiSalDPT in several bases. Examination of the NiSalDPT-pyridine system (Figure 3) showed that the ratios of α:β shifts (3.56) are similar to those

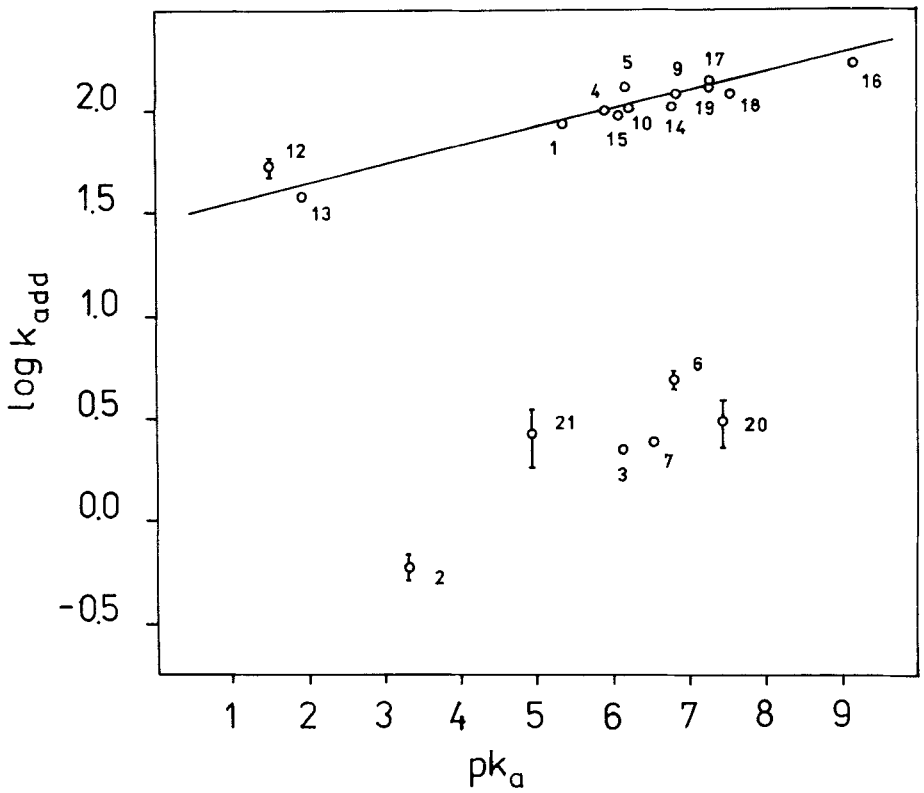

FIGURE 2 Relationship between log K_{add} values for NiSalDPT-base adducts and pK_a of bases; numbers labelling the experimental points are the same as in Table I.

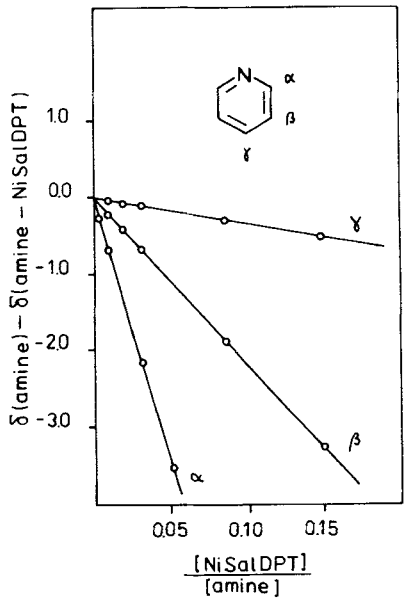

FIGURE 3 Shifts in the ^1H nmr spectrum of pyridine induced by incremental addition of NiSalDPT.

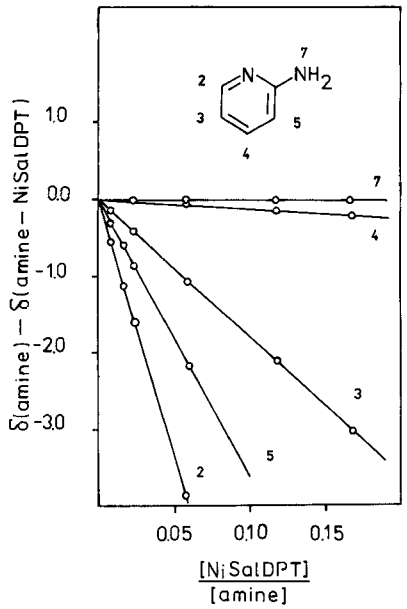

FIGURE 4 Shifts in the ^{1}H nmr spectrum of 2-aminopyridine induced by incremental addition of NiSalDPT.

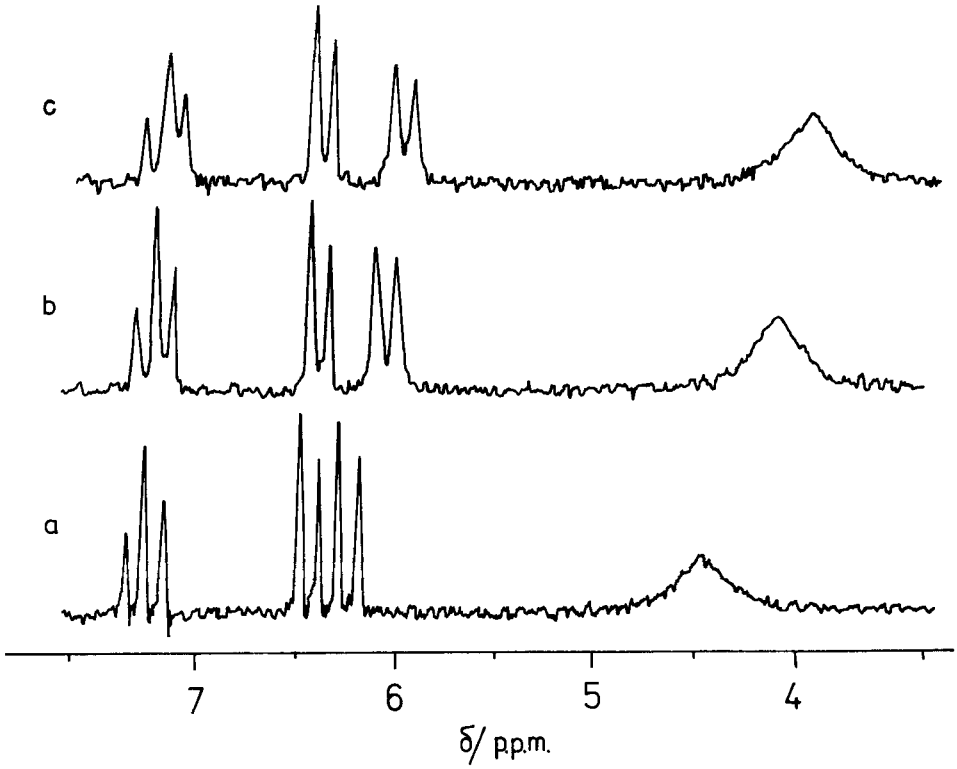

FIGURE 5 Changes in the ^{1}H nmr spectrum of 2-amino-6-methylpyridine induced by NiSalDPT; mol ratio of NiSalDPT to base is a, 0; b, 0.14; c, 0.21.

(3.40) reported by Happe and Ward[4] for pyridine coordinated to nickel(II) acetylacetonate. The downfield shifts and their attenuation in the latter adduct had been interpreted in terms of contact interactions and the σ-mechanism involving transfer of unpaired spin density into orbitals of the coordinated pyridine.[4] Similar changes in shifts of carbon-bonded rotons occur in 2-aminopyridine (Figure 4). Moreover the addition of NiSalDPT does not change the position of the amino group signal in this compound. The downfield shift of the carbon-bonded proton resonances and the rapid attenuation as the number of bonds between a given proton and the heterocyclic nitrogen increases, together with the above observation suggests that the preferred binding site in 2-aminopyridine is the nitrogen atom of the heterocyclic ring. Different behaviour has been observed for 2-amino-6-methylpyridine. The signal of amine protons of this compound is shifted considerably upfield while those of protons bonded to carbon atoms 3 and 5 are shifted unequally so that two well separated doublets appear (Fig. 5). The direction of shifts of the amino and aromatic resonances (Figure 6) is the same as that observed in the NiSalDPT-4-methylaniline system (Figure 7). It had been noted[5] that a strong upfield shift of amine protons in nickel complexes is diagnostic of amine-nickel bonding. Thus, on the basis of the induced shifts, we have assumed that coordination of 2-amino-6-methyl-pyridine to the nickel atom in NiSalDPT occurs *via* the primary amino group. The upfield shift of aromatic protons in 2-amino-6-methylpyridine may arise if the contact shift is dominated by interaction with unpaired electrons in the π-system of the ligand. The d^8 configuration of Ni(II) in a ligand field of O_h, D_{4h} or C_{4v} symmetry places the unpaired electron in orbitals of σ symmetry and no spin density would be expected to arise in the ligands as a result of π bonding with the nickel ion. The hypothesis that spin density does occur in the π-orbitals of ligands coordinated to NiSalDPT suggests that the actual complex formed has symmetry low enough that the unpaired electrons on the nickel may enter orbitals capable of π-bonding to the ligands.

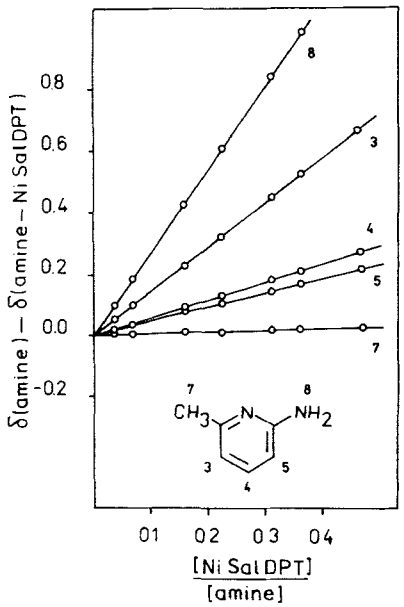

FIGURE 6 Shifts in the ^{1}H nmr spectrum of 2-amino-6-methylpyridine induced by incremental addition of NiSalDPT.

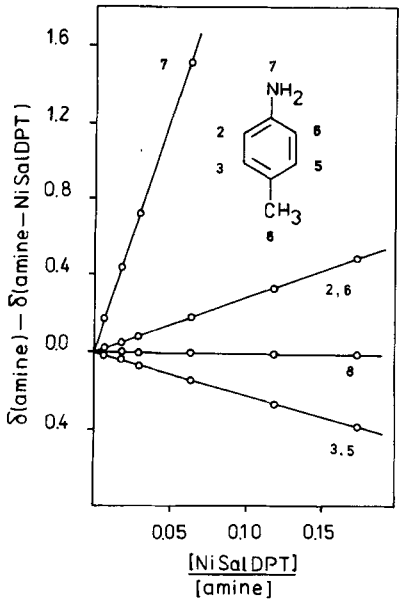

FIGURE 7 Shifts in the ^1H nmr spectrum of 4-methylaniline induced by incremental addition of NiSalDPT.

FIGURE 8 Sections of infrared spectra of a, NiSalMeDPT — 2-aminopyridine crystalline adduct; b, free 2-aminopyridine.

2-Aminopyridine forms 1:1 crystalline adducts with NiSalDPT and its methyl derivative NiSalMeDPT. The infrared spectrum of the NiSalMeDPT-2-aminopyridine adduct in the 3100–3500 cm^{-1} region as compared with that of free base shows that complexation results in a distinct low-frequency shift of N–H vibrations (Figure 8). These changes in the ir spectrum suggest the involvement of the amino group in bonding in the NiSalMeDPT complex. The interaction may compensate for the impairment of stability caused by the steric effect and influence the values of adduct formation constants for NiSalDPT adducts with 2-aminopyridine, 2-amino-3-methyl-pyridine, 2-amino-4-methylpyridine and 2-amino-5-methylpyridine.

ACKNOWLEDGEMENT

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