

New route to bimetallic imidazolate-bridged complexes

V. Spin delocalization in pyridine adducts of mononuclear and dinuclear nickel(II) complexes: a ^1H NMR study

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Abstract

This paper is devoted to the adducts resulting from axial coordination of pyridine to the nickel ions present in mononuclear imidazole complexes and their dinuclear imidazolate bridged homologs. Due to their paramagnetic behaviour, these compounds are amenable to an NMR characterization via the investigation of their isotropic shifts. The shifts pattern observed suggests that spin delocalization mechanisms are operative through a combination of delocalization into the ligand σ -HOMO and π -HOMO. The CH downfield shifts of the imidazole moiety are suggestive of a direct σ -spin delocalization while the 1-CH_3 and 2-CH_3 upfield shifts can be attributed to polarization effects. Furthermore, the 2MeImH complex does not behave as the other imidazole complexes since the corresponding diadducts present a lower amount of overall delocalization.

Introduction

We have previously reported spectroscopic and magnetic data for a novel type of homo- and heterodinuclear copper and nickel complexes with imidazolate bridges [1, 2]. Their properties have been compared to those of the related mononuclear complexes $[\text{AENiImH}]^+$. The latter complexes may react with an excess of pyridine (or imidazole) to form $[\text{AENiImH}\cdot 2\text{B}]^+$ diadducts ($\text{B} = \text{Py}, \text{ImH}$) by axial ligation of two molecules of base B while the dinuclear complex $[\text{AENiImNiAE}]^+$ yields a diadduct at only one metal centre since, in a large excess of Py or ImH, the limiting value of the magnetic moment per binuclear unit is 3.1 ± 0.1 BM, which is the value expected for one nickel ion in the high-spin state.

We did not succeed in isolating any of these adducts, presumably because of their low intrinsic stability. Due to their paramagnetic behaviour they are amenable to an NMR characterization via an investigation of their isotropic shifts. The present paper is devoted to an analysis of the data obtained for some mononuclear complexes (Ia, Ib, Ic in Fig. 1) involving imidazole (ImH), 1-methylimidazole (1MeIm), 2-methylimidazole (2MeImH), 5-methylimidazole (5MeImH) and two related dinuclear com-

plexes (IIa, IIc). These results will be compared with those obtained for a type III complex [3].

Analysis of the experimental data

From the spectra recorded in acetone- d_6 with increasing amounts of pyridine- d_5 , it appears that all the ^1H nuclei of the (AE) and (ImH) moieties are affected by isotropic shifts. In four instances, undeuterated pyridine was used but in a limited range of concentration since a large excess of base obliterates the imidazole signals. Another difficulty originates in the low stability of the adducts. Owing to the rapid exchange rate of pyridine, only averaged spectra over the diamagnetic complexes and their paramagnetic adducts are observed. In every case, they comprise a large contribution from the diamagnetic entity.

The dependence of the ^1H shifts of $[(\text{AENi})_2 2\text{MeIm}]^+$ on the molar fraction of added pyridine is represented in Fig. 2. Similar curves are obtained from all the complexes investigated.

A detailed analysis of these experimental data is not straightforward since for each proton (i) the observed shift $[\delta_0(i)]$ represents a weighted average

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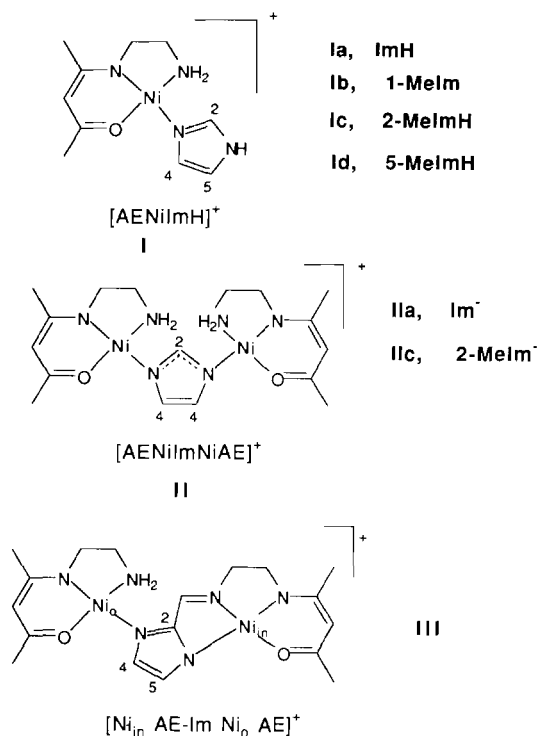
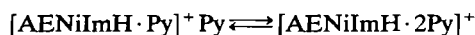
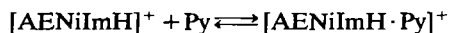


Fig. 1. Schematic structure of monomeric and dimeric species with the numbering of the different nickel compounds.

of the shifts characterizing the diamagnetic complex [$\delta_1(i)$] and the mono- and diadducts [$\delta_{1/1}(i)$] and [$\delta_{1/2}(i)$], respectively.

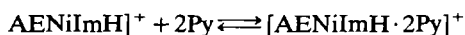
$$\delta_0(i) = p_1 \delta_1(i) + p_{1/1} \delta_{1/1}(i) + p_{1/2} \delta_{1/2}(i)$$

In this model, the system is described by two formation constants ($K_{1/1}$ and $K_{1/2}$) related to the following equilibria



and we are confronted with the problem of determining two sets of limiting shifts ($\delta_{1/1}(i)$ and $\delta_{1/2}(i)$) and two equilibrium constants.

At this stage, it may be noted that the optical spectra of the systems investigated are devoid of any absorption attributable to the monoadduct species $[\text{AENiImH} \cdot \text{Py}]^+$ suggesting that a one-step process



*Visible spectra only show bands attributable to square planar or hexacoordinated nickel centres. The band at 1500 nm characterizing the monoadducts, such as $[\text{AENiImH} \cdot \text{Py}]^+$ was not observed [4].

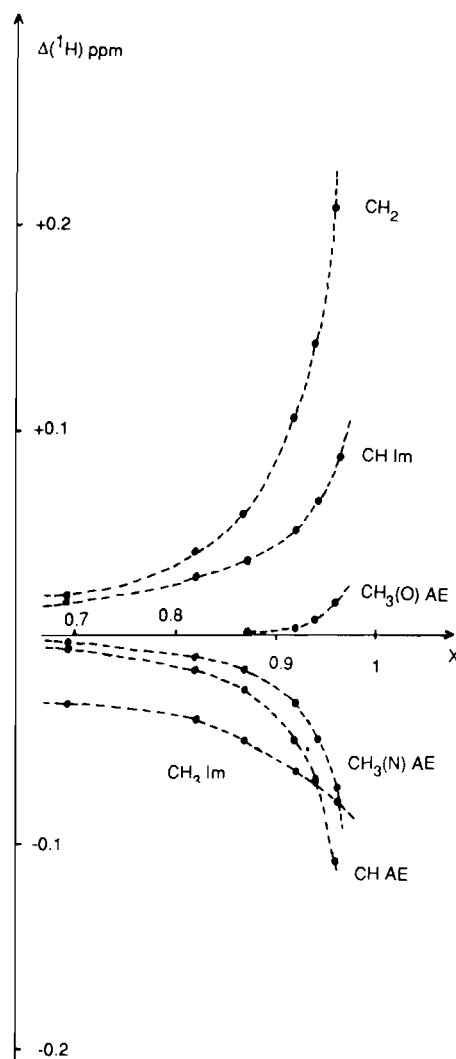


Fig. 2. Variations of the isotropic shifts $\Delta(\text{ppm})$ for the different protons of $[(\text{AENi})_2\text{MeIm}]^+$ as a function of the added amount of pyridine ($X = [\text{Py}]/([\text{Py}] + [\text{complex}])$).

characterized by a constant K , could be assumed in the analysis of the experimental data. In this instance, the concentration in the diadduct is just exactly equal to the concentration in paramagnetic species which can be independently evaluated from magnetic susceptibility measurements. Finally, a joint use of NMR and magnetic data may allow an easy determination of the limiting shifts, $\delta_{1/2}(i)$, attributable to the diadducts and the formation constants (K) characterizing the one-step process.

For each system, it may be convenient to consider the ratios of the limiting shifts for the various protons, $\delta_{\text{H}}(i)$ to the shifts of one particular proton, the

TABLE 1. Observed shifts ($\delta_{1/2}$) and normalized shifts $\Delta(i)$ for $[\text{Ni}_{\text{in}}\text{AE}-\text{ImNi}_{\text{o}}\text{AE}]^+$ (III)

Attribution		$\delta_{1/2}$ (ppm)	$\Delta(i)^a$
CH ₃	OCCH ₃ (o)	1.82	0.03
	OCCH ₃ (in)	2.02	0.00
	NCCCH ₃ (o)	2.13	-0.13
	NCCCH ₃ (in)	2.22	-0.02
CH ₂	NCH ₂ (in)	3.88	-0.05
	H ₂ NCH ₂ (o)	2.71	1.00
	NCH ₂ (o)	3.42	0.82
CH	CH(o)	5.22	-0.23
	CH(in)	5.31	0.00
	CH(5)(in)	6.84	0.26
	CH(4)(in)	7.25	
	N=CH(in)	8.50	-0.14

^aThe Δ values are normalized so that $\Delta(\text{H}_2\text{NCH}_2(\text{o})) = 1.00$ ppm.

methylene protons H₂N-CH₂ in the present case. These ratios $\Delta(i) = \delta_{1/2}(i)/\delta_{1/2}(\text{CH}_2)$, do not depend on the constant K and are directly evaluated from the NMR spectra. Furthermore, they are equal to the ratios of the related hyperfine coupling constants.

As for the dinuclear complexes [5], there is an additional difficulty. Indeed, each ¹H spectrum comprises one set of signals although the magnetic and spectroscopic (ligand field spectra) data show that diadduct formation is restricted to one metal centre. Therefore, the observed shifts result from a dynamic exchange process between $[(\text{AENi})_{\text{in}}(2\text{Py})\text{Im}(\text{AENi})_{\text{o}}]^+*$ and $[(\text{AENi})_{\text{in}}\text{Im}(\text{AENi})_{\text{o}}(2\text{Py})]^+$. To obtain the shifts attributable to the complexed moiety, for instance $(\text{AENi})_{\text{in}}(2\text{Py})\text{Im}$, we have to evaluate the shifts induced by this moiety on the uncomplexed part, $(\text{AENi})_{\text{o}}$, of the molecule. Such an evaluation can be performed by considering the type III complex [3] which displays two distinguishable (AE) entities). For this complex, diadduct formation only occurs as the outer site, $(\text{AENi})_{\text{o}}\text{Im-AE}$ (Fig. 1) and the isotropic shifts attributable to the nuclei of the adduct $[\text{NiAE}-\text{Im}(\text{NiAE})_{\text{o}}(2\text{Py})]^+$ are reported in Table 1. Obviously, the effects exerted by the paramagnetic centre $(\text{NiAE})_{\text{o}}(2\text{Py})$ on the remote part of the molecule are very weak except for the CH₂ groups. There is an additional difficulty in the case of $[(\text{AENi})_22\text{MeIm}]^+$. For this complex, the signals of the 2MeIm moiety become broad and hardly discernible when the ratio $[\text{Py}]/$

$[\text{Py}] + [\text{complex}]$ is greater than 0.8. In this instance it is better to evaluate first the related $\Delta(i)$ which are then used to calculate the $\delta_{1/2}(i)$ values. The values ($\delta_{1/2}(i)$ and $\Delta(i)$) characterizing the mono- and dinuclear complexes of type I and II are reported in Table 2.

Discussion

The experimental isotropic shifts generally arise from a contact contribution and a dipolar contribution. For octahedrally coordinated nickel(II) ion with an isotropic ³A₂ ground state, the dipolar term is negligible and the shifts can be considered as merely contact in origin. In the present complexes, this approximation is further supported by the observation that the most important shifts are related to the signals which suffer the larger broadening**.

Considering first the normalized shifts, it appears that virtually the same pattern, $\Delta(i) = \delta_{1/2}(i)/\delta_{1/2}(\text{CH}_2)$, is observed in all the complexes for the protons of the AE moiety surrounding the high-spin nickel atom. The most important shift ($\Delta = 1$) is related to the methylenic protons H₂N(CH₂) which move downfield as do the ¹H nuclei of the other methylenic group, N(CH₂), but to a lesser extent ($\Delta \approx 0.95$). Upfield shifts are observed for the CH ($\Delta \approx -0.26$) and NCCCH₃ protons ($\Delta \approx -0.17$) while the OCCH₃ protons are marginally affected. This shift pattern is strongly reminiscent of the one reported by La Mar [6] for β -ketoimine nickel complexes, suggesting that, in both series, similar spin-delocalization mechanisms are operative, viz. a combination of delocalization into the ligand π -HOMO and σ -HOMO. A similar conclusion can be gained from the data of INDO calculations [7] performed on a 'ligand fragment', H₃C-N=C(CH₃)-CH-C(CH₃)-O⁻, which is almost identical to our AE ligand.

Interestingly, these data predict that parallel spin density in the σ -system would cause opposite shifts for OCCH₃ (downfield) and NCCCH₃ (upfield). However, these shifts are expected to display similar magnitudes while the values reported in Table 2 are markedly different. Furthermore, this transfer is expected to deshield the CH proton which actually suffers an upfield shift. It is obvious that at least one additional mechanism needs to be considered to justify the observed shifts pattern. A likely candidate is a spin transfer into the π -HOMO. According to the results disclosed in ref. 7, parallel spin density in the AE π -HOMO would result in upfield shifts of similar magnitude for the two methyl groups, a

*o for outer, in for inside, on analogy of the type III complex.

**In a situation where the contact mechanism dominates, the signal widths are expected to correlate with the square of the isotropic shifts due to the dependence of both quantities on the hyperfine coupling constant.

TABLE 2. Observed shifts $\delta_{1/2}(t)$ and normalized shifts $\Delta(t)$ of the different complexes

	[(AENi) ₂ L] ⁺																		
	L = ImH			L = 1MeIm			L = 2MeImH			L = 5MeImH			L = Im ⁻			L = 2MeIm ⁻			
	$\delta_{1/2}(t)$	$\Delta(t)$		$\delta_{1/2}(t)$	$\Delta(t)$		$\delta_{1/2}(t)$	$\Delta(t)$		$\delta_{1/2}(t)$	$\Delta(t)$		$\delta_{1/2}(t)$	$\Delta(t)$		$\delta_{1/2}(t)$	$\Delta(t)$		
AE																			
OCCH ₃	0.9	0.0(2)		0.9	0.0(2)		0.3	0.0(2)		0.7	0.0(2)		0	0		0	0		0
NCCH ₃	-6.0	-0.2		-6.1	-0.1(5)		-3.1	-0.1(5)		-5.8	-0.3		-2.8	-0.2		-1.3	-0.2		-0.2
H ₂ NCH ₂	35.0	1.0		37.3	1.0		18.9	1.0		34.6	1.0		14.5	1		6.2	1		1
NCH ₂	33.3	0.9		32.5	0.9		16.4	0.8(5)		31.5	0.9		11.5	0.8					
CH	-9.0	-0.2(5)		-9.7	-0.2(5)		-5.1	-0.3		-9.2	-0.2(5)		-4.3	-0.3		-2.0	-0.3		-0.3
Im																			
CH ₃				-0.7(5)	-0.0(2)		-3.0	-0.1(5)		3.5	0.1								
CH(2)				18.7	0.5					18.0	0.5		8.7	0.6					
CH(4)				25.2	0.7(5)		9.8	0.5		23.2	0.7		11.0	0.7(5)					
CH(5)				20.5	0.5(5)		4.2	0.2					11.0	0.7(5)					
Py																			
CH(2)				3.5	0.1		4.5	0.2(5)					1.8	0.1					
CH(3)				2.2	0.0(5)		2.6	0.1(5)					1.2	0.0(8)					
CH(4)				1.9	0.0(5)		1.5	0.1					0.9	0.0(5)					

*See text.

somewhat larger upfield shift for CH and an important downfield for CH_2 . Thus, a combination of spin delocalization into the σ -HOMO and the π -HOMO accounts for the observed shifts, at least qualitatively. In this instance, the small shift ($\Delta = 0.02$) of $OCCH_3$ may result from an approximate cancellation of two opposite effects, suggesting that amount of σ -delocalization is more important than in the previous examples [6, 7]. Interestingly, a detailed INDO analysis [8] of the shifts observed for $Ni(Acac)_2 \cdot 2Py$ shows that the major delocalization is into the ligand HOMO with π -symmetry although a significant contribution from the next highest orbital which is a σ -type orbital is also present. Delocalization in the σ -system is not surprising but, as noted by others [6, 7], the conclusion that unpaired spin density is delocalized into the ligand π -HOMO is rather unexpected since significant overlap of this orbital with the half-filled d-orbitals of the nickel ion is not likely to occur in an octahedral geometry. It has been suggested that unpairing of the t_{2g} electrons could be caused by spin-orbit coupling and/or lowering of the symmetry that would remove the orthogonality between the metal d-orbitals of σ -symmetry and the ligand π -orbitals.

As for the imidazole moiety, examination of Table 2 shows that all the CH experience downfield shifts which are suggestive of a direct σ -spin delocalization. This is further supported by the fact that the magnitudes of the shifts at H(4) and H(5) are larger than at H(2), in accordance with the pattern of σ -orbital spin densities obtained by INDO calculations [9]. The behaviour of the methylic protons is more surprising. Indeed, the protons of the 5-Me group move downfield as is usually the case for a σ -spin delocalization mode but the protons of the 2-Me and 1-Me groups actually suffer upfield shifts which could reflect the occurrence of some negative π -spin density. It may be noted that π -spin density may or may not be related to any direct π -spin delocalization. Indeed, an indirect mechanism of spin polarization has been postulated for substituted pyridines coordinated to a nickel(II) centre [10]. Upfield contact shifts have also been observed for the methyl protons in 2,4-MeImH complexes of ferrous porphyrins and attributed to polarization effect and/or direct interaction with the porphyrin π -system [11].

Regarding the pyridine protons, we observe that they move downfield in complexes $[AENiImH \cdot 2Py]^+$, the magnitude of the shifts decreasing from H(2) to H(3) and H(4), in accordance with direct σ -delocalization of parallel spins [10].

In contrast to the normalized shifts $[\Delta(i)]$ which virtually display the same pattern in all the complexes

under investigation, consideration of the limiting shifts $\delta_{1/2}(i)$ attributable to the diadducts points to clear distinctions (a) between **Ic** and the other complexes in the mononuclear series and (b) between the mononuclear species (**Ia**, **Ic**) and their dinuclear homologs (**IIa**, **IIc**).

In a previous paper [2], we have suggested that a steric interaction could be operative between a 2- (or 4-)methyl substituent on the imidazole ring and the $OCCH_3$ group of AE to prevent coplanarity of the imidazole plane with the AENi plane while coplanarity would be closely approached in the case of unsubstituted imidazole [1] and 1- and 5-methylimidazoles. Such a variation of the dihedral angle may affect a possible interaction [12] between the metal d-orbital and the imidazole π_1 (HOMO) orbital which has mainly carbon 2p(π) character [13, 14]. This could result in a direct modification of spin-delocalization pattern on the imidazole ring while an indirect modification [15] would affect AE.

Regarding the difference between mono- and dinuclear complexes, it could originate in the substitution of an anionic ligand (Im^-) for a neutral one (ImH) with a subsequent decrease of the ligand contribution to the σ -orbital containing the spin. As previously, the AE moiety would be indirectly affected.

It may be noted that whatever the origin of the shift (δ) differences, it is not clear why they do not significantly alter the Δ values. Obviously, a more satisfactory analysis of the delocalization modes awaits an elaborated theoretical model involving simultaneously the metal and ligand orbitals.

The most important conclusion is that, as previously noted, the 2MeImH ligand does not behave as the other imidazole ligands, since the corresponding diadducts present a lower amount of overall delocalization.

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