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New Route to Bimetallic Imidazolate-bridged Complexes. II. NMR Study of Dinickel Complexes. Importance of the Non-bonded Interactions

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Abstract

A series of methyl-substituted imidazole complexes of the (AENi) moiety (AE being the anionic form of 7-amino-4-methyl-5-aza-3-hepten-2-one) and of the related dinickel imidazolate-bridged complexes was prepared. ^{1}H and ^{13}C NMR data at 295 and 203 K are reported for the free ligands and their mononuclear and dinuclear complexes. Consideration of the whole set of data with a particular emphasis on the influence of the temperature points to the importance of non-bonded interactions. Complexing the (AENi) moiety with 4/5-MeImH yields a mixture of the two mononuclear isomers, $[(AE)Ni4\text{-}MeImH]^{+}$ and $[(AE)Ni5\text{-}MeImH]^{+}$, the latter being largely predominant.

Introduction

In a previous paper [1] we reported a method to build homo- and heterodimetallic complexes involving an imidazolate bridge between the two metals. This method relies on a terdentate Schiff base, 7-amino-4-methyl-5-aza-3-hepten-2-one (abbreviated as AEH in the following) which allows the obtention of four-coordinated complexes, $[(AE)MImH]^{+}$, involving a non-deprotonated imidazole (ImH) as complementary ligand. Deprotonation of ImH offers the possibility of coordinating a second metal through the outer nitrogen of the imidazolate [Im^{-}] to yield a binuclear complex.

The present paper is devoted to a detailed NMR study of some dinickel imidazolate-bridged complexes and their mononuclear precursors. The frequent occurrence of imidazole derivatives in biologically important complexes has given a large impetus to NMR characterization of this type of ligand. However it is generally accepted that the NMR spectra of transition-metal complexes with heterocyclic ligands are difficult to interpret due to many competing effects [2]. Because of their relatively simple structure and the possibility of comparing mono- and dinuclear homologs, the present complexes are expected to give useful informations about the main factors governing the NMR behaviour of the ImH and Im^{-} ligands.

An example of the mononuclear complexes under investigation is given in Fig. 1 along with the numbering scheme used in the text and in the tables. In the following the ligands are represented by Py (pyridine), 2-Pic (2-picoline), ImH (imidazole), Im^{-} (imidazolate), 1-MeIm (1-Methylimidazole), 2-MeImH (2-Methylimidazole), 4-MeImH (4-Methylimidazole), BzImH (Benzimidazole).

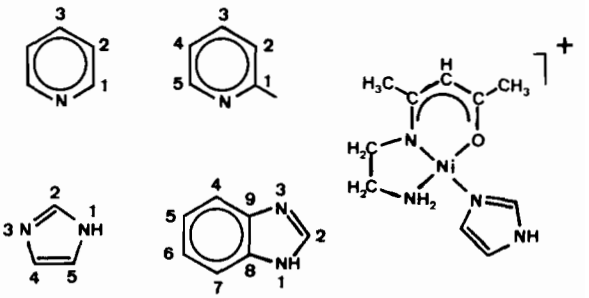

Fig. 1. Schematic structure of the monomeric species $[(AE)NiImH]^{+}$ and numbering of the nitrogen heterocycles.

Experimental

Synthesis of Ligands and Complexes

Reagents and solvents used were commercially available reagent quality. The ligand, 7-amino-4-methyl-5-aza-3-hepten-2-one, abbreviated AEH in the following, was prepared as described earlier [2]. Substitution of 2,4-pentanedione for 2,4-hexanedione yields the ligand 8-amino-5-methyl-6-aza-4-octen-3-one, abbreviated AE(Et)H.

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([(AE)Ni2-Pic]ClO$_4$) (2)

This compound was prepared in the same way as ([AE)NiPy]ClO$_4$) (**1**) [3] (80% yield). *Anal.* Calc. (Found) for $C_{13}H_{20}N_3ClNiO_5$: C, 39.85(39.96); H, 5.11(5.20); N, 10.73(10.70); Cl, 9.07(9.20); Ni, 14.81(14.75)%.

([(AE)NiImH]ClO$_4$) (3)

To a 7×10^{-3} M solution of AEH in methanol (40 ml) was first added with stirring the equivalent amount of a MeOH solution of NaOMe and then another MeOH solution (30 ml) containing 2.57 g of $Ni(ClO_4)_2 \cdot 6H_2O$ and 0.5 g of ImH. The orange solution obtained quickly gave an orange precipitate which was filtered, washed with cold methanol, ether, and then dried (70% yield). *Anal.* Calc. (Found) for $C_{10}H_{17}N_4ClNiO_5$: C, 32.74(32.85); H, 4.64(4.75); N, 15.28(15.12); Cl, 9.69(9.80); Ni, 15.82(15.80)%. The same experimental procedure was used for the other monomeric compounds.

([(AE)Ni1-MeIm]ClO$_4$) (4)

70% yield. *Anal.* Calc. (Found) for $C_{11}H_{19}N_4ClNiO_5$: C, 34.69(34.45); H, 4.99(4.95); N, 14.72 (14.50); Cl, 9.33(9.40); Ni, 15.24(15.15)%.

([(AE)Ni2-MeImH]ClO$_4$) (5)

65% yield. *Anal.* Calc. (Found) for $C_{11}H_{19}N_4ClNiO_5$: C, 34.69(34.44); H, 4.99(4.91); N, 14.72 (14.64); Cl, 9.33(9.45); Ni, 15.24(15.20)%.

([(AE)Ni4/5-MeImH]ClO$_4$) (6)

63% yield. *Anal.* Calc. (Found) for $C_{11}H_{19}N_4ClNiO_5$: C, 34.69(34.75); H, 4.99(5.05); N, 14.72 (14.70); Cl, 9.33(9.48); Ni, 15.24(15.30)%.

([(AE)NiBzImH]ClO$_4$) (7)

Adding BzImH to a MeOH solution of **1** in a 1:1 ratio and concentrating the solution yields **7** (80%). *Anal.* Calc. (Found) for $C_{14}H_{19}N_4ClNiO_5$: C, 40.34 (40.23); H, 4.56(4.60); N, 13.44(13.40); Cl, 8.52 (8.70); Ni, 13.92(13.82)%.

([(AE(Et))NiImH]ClO$_4$) (8)

This compound was prepared in the same way as **1** (65% yield). *Anal.* Calc. (Found) for $C_{11}H_{19}N_4ClNiO_5$: C, 34.69(34.65); H, 4.99(5.00); N, 14.72 (14.53); Cl, 9.33(9.07); Ni, 15.24(15.04)%.

([(AE)NiImNi(AE)]ClO$_4$) (9)

0.5 g of **3** was put in 30 ml of MeOH. Addition of 0.25 ml of a 5.4 M MeOH solution of NaOMe brings about the dissolution of the monomeric complex. A few minutes later, an orange–red precipitate appeared, which was filtered, washed with MeOH, ether and dried (85% yield). *Anal.* Calc. (Found) for $C_{17}H_{29}N_6ClNi_2O_6$: C, 36.14(35.97); H, 5.14(5.08); N, 14.88(14.60); Cl, 6.29(6.29); Ni, 20.55(20.73). The other dimeric species were synthesized in a similar way.

([(AE)Ni2-MeImNi(AE)]ClO$_4$) (10)

80% yield. *Anal.* Calc. (Found) for $C_{18}H_{31}N_6ClNi_2O_6$: C, 37.34(37.15); H, 5.36(5.30); N, 14.52 (14.45); Cl, 6.14(6.01); Ni, 20.05(20.20)%.

([(AE)Ni4-MeImNi(AE)]ClO$_4$) (11)

In this case, we employed BuOH instead of MeOH in order to precipitate the product (60% yield). *Anal.* Calc. (Found) for $CI_8H_{31}N_6ClNi_2O_6$: C, 37.34 (37.10); H, 5.36(5.40); N, 14.52(14.50); Cl, 6.14 (6.05); Ni, 20.05(19.91)%.

([(AE)NiBzImNi(AE)]ClO$_4$) (12)

80% yield. *Anal.* Calc. (Found) for $C_{21}H_{31}N_6ClNi_2O_6$: C, 41.01(40.82); H, 5.04(4.92); N, 13.67 (13.75); Cl, 5.78(5.60); Ni, 18.88(18.70)%.

Safety note. The compounds reported here were isolated as perchlorate salts. We have worked with these compounds in several organic solvents without incident, and, as solids, they seem to be reasonably stable to shock and heat. Nevertheless, the unpredictable behavior of perchlorate salts [4] necessitates extreme caution in their handling.

Physical Measurements

Microanalyses were performed by the Service Central de Microanalyse du CNRS, Lyon, France. ^1H and ^{13}C NMR spectra were recorded at ambient (295 K) and low temperature (203 K) with a Brucker WM 250 spectrometer. Gated broad-band decoupling $\{^1H\}^{13}C$ experiments with selective proton irradiation during acquisition were performed in some instances at ambient or low temperature.

All chemical shifts (^1H and ^{13}C) are given in ppm *versus* TMS using CD_3COCD_3 as a solvent.

^{13}C and ^1H NMR Results

^{13}C Resonances, AE Moiety

The ^{13}C spectrum (^1H decoupled) of the AE moiety in the mono- and dinuclear complexes displays seven signals which are readily attributed by a joint utilization of non-decoupled spectra and chemical shifts criteria to two CH_3 (20.7, 23.1 ppm), two CH_2 (43.9, 54.3 ppm), one CH (99.9 ppm) and two quaternary carbon nuclei (166.5, 175.3 ppm). However complementary experiments are needed to differentiate the two methyl and the two methylene groups. In this last case, deuteriation of the mononuclear complex (**3**) results in changing the resonance at 43.9 ppm from a singlet into a triplet due to J^2(DNC) coupling (7 Hz). The resulting assignment, *i.e.* $\delta(CH_2NH_2) = 43.9$ ppm and $\delta(CH_2N) = 54.3$

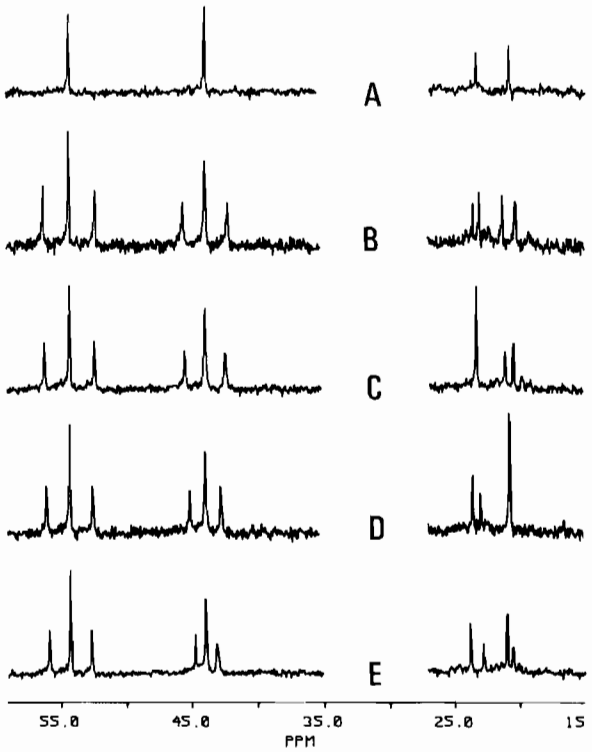

Fig. 2. Evolution of the methyl and methylene signals of the ^{13}C NMR spectra of $[(AE)NiPy]^+$ according to a selective proton irradiation study. A, broad band decoupling; C, effect of irradiation of the methyl ^1H resonance at 1.83 ppm; D at 2.15 ppm. B and E show the effect of irradiation of the methyl ^1H area around 1.6 ppm and 2.3 ppm respectively.

ppm, is supported by selective decoupling of the related ^1H signals which are confidently attributed on the basis of their multiplicity. Regarding the methyl resonance, use of selective proton decoupling (Fig. 2) shows that the ^1H signal at 1.86 ppm attributed to (CH_3CO) must be related to the ^{13}C signal at 23.1 ppm. Conversely, upon irradiation of the ^1H resonance at 2.13 ppm, the quadruplet centered at 20.7 ppm in the ^{13}C spectrum collapses.

^{13}C Resonances, ImH Ligands and Analogs

As noted in different papers, the major difficulty in attributing the ^{13}C spectra of ImH concerns the C(4) and C(5) nuclei. For the free ligand, the two resonances collapse in solution due to a rapid tautomeric equilibration [5, 6]. However, solid state spectra (CPMAS) [7] show separate signals at 126.8 and 115.3 ppm attributed to C(4) and C(5) respectively, the C(2) resonance appearing at 136.3 ppm. Under similar conditions (solid-state sample, CPMAS technique*) the imidazole moiety of **3** yields three signals at 138.5, 125.7 and 118.5 ppm whereas two signals (142.4 and 124.2 ppm) are observed in the case of the dinuclear complex **9**. In this last instance C(4) and C(5) are obviously equivalent, their chemical shift $\delta = 124.2$ ppm may be regarded as characteristic of a carbon nucleus, namely C(4) and/or C(5), adjacent to a coordinated nitrogen atom. Therefore, the resonance observed at 125.7 ppm in the solid-state spectrum of **3** is likely attributable to C(4). By extension to solution spectra, the data quoted in Table I are obtained. This assignment is further supported by considering the complexation shifts $\Delta\delta(=\delta$ complex $-\delta$ ligand) which, for **3**, are found equal to 2.2 ppm [C(2)], -1.0 ppm [C(4)] and 3.2 ppm [C(5)]. These effects are very similar to those reported for related cobalt complexes [8].

The spectra of the complexes involving benzimidazole are attributed in relation with the published data [9] for the benzimidazolium ion.

The complexes prepared from 4-MeImH deserve further comments. The ^1H spectrum of the mononuclear species points to the presence of two isomers **6a** and **6b**, *i.e.* $[(AE)Ni5\text{-}MeImH]^+$ and $[(AE)Ni4\text{-}MeImH]^+$, the former isomer being largely predominant. The signals related to this form are clearly observed in the ^{13}C spectrum at 136.3, 123.1, 127.3 and 9.0 ppm. From their δ values, the signals at 136.3 and 9.0 ppm may be attributed to C(2) and (CH_3) respectively. This is confirmed by the coupling patterns observed in the ^1H-coupled spectrum which, in addition, allows the signal at 123.1 and 127.3 ppm to be assigned to a methine group [C(4)] and a quaternary carbon [C(5)] respectively. Signals attributable to the 4-MeImH isomer **6a** are observed at 12.5 ppm (CH_3) and 127.1 ppm [C(5)H]. Due to its intrinsic low intensity the resonance of the quaternary carbon C(4) is not detected. For the dinuclear complex **11**, there is no possibility of isomerism. However, the inequivalence of the two AE ligands is clearly demonstrated by the observation of two (CH_3CO) and two (CH_2) signals (*vide infra*).

It may be noted that for the mononuclear complexes, the ^{13}C signals of the AE moiety are practically not affected by varying the temperature but the width of the ImH signals decreases markedly as the temperature is lowered. Typically $\Delta\nu_{1/2}$ varies from 400 Hz at 295 K to 150 Hz at 205 K whereas the chemical shifts remain unaltered. This behaviour generally indicates that, over a large temperature range, the molecule predominantly exists in a preferred conformation. The spectra of the dinuclear complexes are not temperature dependent.

^1H Resonance, AE Moiety

Analysis of the ^1H spectra of the AE moiety (*cf.* Table II), is quite straightforward. A singlet at *ca.* 5 ppm corresponds to the methine proton. The methylene (CH_2N) resonance appears as a triplet due

*The CP-MAS spectra were recorded on a Bruker CXP-300 spectrometer working at 75.46 MHz by Dr M. Ziliox (Bruker Physik AG) to whom we are greatly indebted: spinning rate, 4–4.5 KHz; spectral width, 31.25 KHz.

TABLE I. ^{13}NMR Data at 295 K and 203 K

Compound	CH_3		CH_2		CH	CN	CO	1	2	3	4	5	6	7	8	9
	CN	CO	NH_2	N												
1	20.8	23.3	43.9	54.3	100.2	166.7	175.2	151.0[d]	125.5[d]	138.6[d]						
2	20.6	22.9	44.1	54.1	100.0	166.7	175.3	160.9 (25.2)[a]	126.3	139.2	122.6	150.9				
3	20.6	23.1	43.9	54.4	100.1	166.5	175.2		137.4[d]		126.8[d]	117.8[d]				
4	20.7	23.2	43.9	54.3	100.2	166.7	175.4	(34.0)[d]	140.1[d]		127.8[d]	122.4[d]				
5	20.6	22.9	43.8	54.1	99.7	166.2	175.2		146.9 (13.5)		127.0	117.4				
7	20.7	22.9	43.9	54.3	99.9	166.4	175.2		143.4[d]		118.5[d]	124.3[d]	124.3[d]	113.6[d]	132.7[d]	139.5[d]
9	20.6	23.3	44.0	53.9	99.7	166.0	175.4		142.1		125.1	125.1				
10	20.6	23.1	43.8	53.7	99.5	165.7	175.5		151.1 (16.8)		125.9	125.9				
11	21.6	23.9	44.7	54.9	100.8	167.5	176.5		142.9		136.8 (13.8)	124.2				
		24.3		55.2												
12[c]	20.6	23.0	44.0	53.9	99.7	166.0	175.4		149.5		116.7	120.8	120.8	116.7	142.1	142.1
3[b]	20.7	23.0	43.4	54.0	99.8	165.9	174.4		137.1		126.4	117.7				
4[b]	20.6	22.9	43.2	54.0	99.9	166.1	174.6	(33.9)	138.9		127.1	121.9				
6a[b]	20.6	22.9	43.3	53.9	99.7	165.9	174.4		136.6		n.o. (12.5)	127.1				
6b[b]	20.6	22.9	43.3	53.9	99.7	165.9	174.4		136.3		123.1	127.3 (9.0)				
7[b]	20.7	22.7	43.5	53.9	99.7	165.9	174.5		143.3		118.1	123.5	124.3	113.1	132.1	139.0

[a]Methyl imidazole resonances in parentheses. [b]Spectra at 203 K. [c]In MeOH d_4. [d]Broad signals.

TABLE II. ^{1}H NMR Data at 295 K

Compound	CH_3		CH_2		CH	NH_2	1	2	3	4	5	6	7
	CO	CN	NH_2	N									
1	1.83	2.15	2.78	3.43	5.26	3.59	9.08[b]	7.72[b]	8.15[b]				
2	1.74	2.15	2.75	3.39	5.23	3.47	(3.91)[a]	7.60	7.99	7.54	9.61		
3	1.88	2.13	2.72	3.41	5.23	3.54	12.06[b]	8.09[b]		7.21[b]	7.32[b]		
4	1.88	2.12	2.74	3.43	5.21	3.48	(3.92)	8.01[b]		7.09[b]	7.33[b]		
5	1.78	2.12	2.66	3.37	5.20	3.29	11.66[b]	(3.08)		7.22	7.39		
6a	1.80	2.12	2.70	3.39	5.22	3.50	11.81[b]	8.39[b]		(2.34)[b]	7.09[b]		
6b	1.87	2.12	2.70	3.39	5.22	3.50	11.81[b]	7.91[b]		6.81[b]	(2.34)[b]		
7	1.75	2.16	2.74	3.44	5.24	3.44	12.45[b]	8.87[b]		8.56[b]	7.52[b]	7.52[b]	7.83[b]
9	1;86	2.08	2.65	3.33	5.17	3.37		7.13		6.63	6.63		
10	1.76	2.07	2.59	3.29	5.14	2.98		(3.46)		6.97	6.97		
11	1.76	2.07	2.63	3.33	5.15	3.05		7.37		(2.64)	6.34		
	1.87			3.31	5.13								
12	1.78	2.17	2.72	3.38	5.23	3.28		8.18		8.17	7.25	7.25	8.17

[a]Methyl imidazole resonances in parentheses. [b]Broad signals.

TABLE III. ^{1}H NMR Data at 203 K

Compound	CH_3		CH_2		CH	NH_2	1	2	3	4	5	6	7
	CO	CN	NH_2	N									
1	1.80	2.14	2.74	3.38	5.28	3.85	9.06	7.77	8.19				
2	1.71	2.14	2.72	3.34	5.26	3.71	(3.87)[a]	7.66	8.03	7.60	9.65		
3	1.86	2.12	2.67	3.37	5.26	3.79	12.35	8.14		7.11	7.48		
4	1.85	2.11	2.64	3.35	5.25	3.80	(3.91)	8.03		7.01	7.39		
5	1.76	2.10	2.61	3.32	5.22	3.53	12.08	(3.03)		7.33	7.40		
6a	1.74	2.11	2.65	3.35	5.22	3.50	11.80	8.47		(2.84)	7.18		
6b	1.85	2.11	2.65	3.35	5.25	3.72	11.80	7.98		6.78	(2.29)		
7	1.73	2.15	2.68	3.39	5.27	3.68	12.77	8.97		8.58	7.56	7.56	7.80
9	1.83	2.06	2.59	3.28	5.21	3.70		7.06		6.58	6.58		
10	1.75	2.05	2.53	3.25	5.19	3.25		(3.36)		6.94	6.94		
11	1.85	2.05	2.58	3.28	5.18			7.35		(2.58)	6.26		
	1.73			3.26	5.15								
12	1.74	2.11	2.67	3.34	5.25	3.57		8.13		8.07	7.25	7.25	8.07

[a]Methyl imidazole resonances in parentheses.

to coupling with the adjacent (CH_2NH_2) group which in turn gives a quintet resulting from coupling with the previous (CH_2N) group and the NH_2, the two coupling constants being almost identical (5 Hz). For the two CH_3 groups an unambiguous assignment is performed via the paramagnetic shifts induced by axial fixation of pyridine onto the nickel: one methyl group suffers a pronounced upfield shift while the other is affected by a feeble downfield shift. If we consider the homologous complex **8** in which the $OCCH_3$ group has been replaced by a OCC_2H_5 group* **11**, we observe that, in both complexes, a methyl signal occurs at practically the same position (2.13 ppm). When pyridine is added this signal moves highfield while the second CH_3 signal in **3** and the CH_3 and CH_2 signals in the ethyl-substituted complex **8** are slightly displaced towards lower fields. The resulting attributions (*cf.* Tables II and III) have been checked by off-resonance decoupling experiments.

^{1}H Resonance, ImH Ligands and Analogs

For the mononuclear complexes involving 1 MeIm, ImH and 2-MeImH, separate H(4) and H(5) resonances are observed at 295 K. The position and width of these resonances are very sensitive to the probe temperature (*vide infra*). In order to appropriately assign these signals, selective heteronuclear (^{1}H, ^{13}C) decoupling experiments have been per-

*When 1,2-diamonoethane reacts with a non-symmetric β-diketone, it has been shown, by a X-ray structure, that the condensation occurred at the β-diketone carbon atom to which the methyl substituent is attached [10].

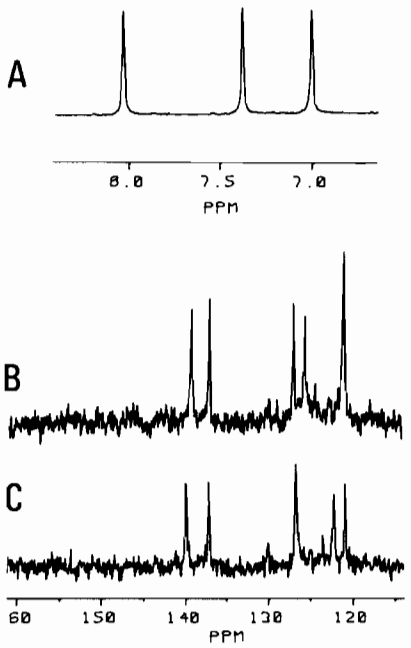

Fig. 3. Selective proton irradiation study of [(AE)Ni1-MeIm]$^+$ at 209 K. A, ^{1}H NMR spectrum of 1-MeIm. ^{13}C NMR spectra after irradiation of: B, the downfield ^{1}H resonance at 7.39 ppm; C, the upfield ^{1}H resonance at 7.01 ppm.

formed. Such an experiment is described in Fig. 3. Irradiation of the proton resonance at 7.39 ppm causes the collapse of the upfield ^{13}C doublet in a single line at 122.4 ppm while irradiation of the proton resonance at 7.01 ppm results in coalescence of the downfield ^{13}C doublet in one single signal at 127.8 ppm. From the known ^{13}C assignment [11], the signals at 7.01 and 7.39 ppm are attributed to H(4) and H(5) respectively. Data with the same interpretation have been obtained for the 2-MeImH mononuclear complexes.

Attribution of the signals for the related dinuclear complexes are straightforward since H(4) and H(5) are structurally equivalent in these species.

Low temperature spectra of the mono and dinuclear complexes prepared from 4-MeImH (**6a**, **6b**, **11**) are characterized by a number of signals higher than expected. Chemical shift criteria show that the $OCCH_3$, CH and NCH_2 of the AE moiety are splitted in both complexes whereas splitting of the imidazole signals only occurs in the mononuclear species. Interestingly, the intensities of the two sets of signals which are almost identical for the dinuclear complex differ markedly for the mononuclear species. Inequivalence of the AE signals in the dinuclear complexes originates in the presence of a methyl substituent at one of the 4- and 5- positions of the Im ring which lowers the overall symmetry of the molecule. It is noteworthy that the major inequivalence occurs at the $OCCH_3$ group. Regarding the mononuclear

TABLE IV. Complexation Shifts (ppm) in the Mononuclear Complexes at 203 K (no exchange)

	H(2)	H(5)	H(4)	(CH_3)
ImH	0.23	0.23	−0.09	
1-MeIm	0.46	0.27	−0.01	0.11
2-MeImH		0.37	0.30	0.60
4-MeImH	0.78	0.30		0.53
5-MeImH	0.29		−0.10	−0.02

complexes the two sets of signals are likely indicative of the occurrence of two isomers, namely [(AE)Ni4-MeImH]$^+$ (**6a**) and [(AE)Ni5-MeImH]$^+$ (**6b**). This is supported by the large difference in intensity of these two sets of signals and the fact that the two $OCCH_3$ are characterized by δ values of 1.74 and 1.85 ppm, respectively, which are almost identical with the values observed for the dinuclear complex **11**. Considering the data in Tables III and IV shows that the $OCCH_3$ resonance appears at 1.73 ± 0.03 ppm in the mono- and dinuclear complexes of 2-MeImH and BzImH and at 1.85 ± 0.02 ppm in the complexes of ImH and 1-MeIm. A similar difference is also observed between the complexes of Py (**1**) and 2-Pic (**2**). The origin of this effect will be considered later but the observed trend suggests that for the 4/5-MeImH complexes, the signals at 1.74 and 1.85 ppm are attributable to the 4-Me and 5-Me isomers respectively. From their relative intensity, it may be inferred that the predominant isomer is the remote isomer, the methyl being located at the 5-position of the imidazole ring.

An important characteristic of the ^{1}H spectra is the great sensitivity of the imidazole signals to the temperature which is in marked contrast with the related cobalt complexes [12] and with the fact that the AE signals are practically not affected over a large temperature range (325 to 205 K). At 295 K the H(4) and H(5) resonance of ImH in **3** are broad ($\Delta\nu_{1/2}$ = 40 Hz) but separated ($\Delta\delta$ = 0.09 ppm). Raising the temperature up to 323 K causes the coalescence of the signals (*cf.* Fig. 4). Lowering the temperature results in increasing the separation between the signals ($\Delta\delta$ = 0.37 ppm at 205 K) and simultaneously decreasing their width ($\Delta\nu_{1/2} \approx 7$ Hz at 205 K). This is the behaviour expected for a tautomeric exchange very similar to that observed for the free ligand but with a very different rate of exchange. In the case of **4**, the presence of a methyl group at N(1) excludes any possibility of tautomerism. However, the H(4) and H(5) signals which are rather broad at 295 K ($\Delta\nu_{1/2} \approx 15$ Hz) become sharper as the temperature is lowered ($\Delta\nu_{1/2}$ = 4 Hz at 205 K) but their separation is little affected. A more complex behaviour is observed for **5** (*cf.* Fig. 5). At 325 K the H(4) and H(5) resonances merge in a broad signal ($\Delta\nu_{1/2}$ =

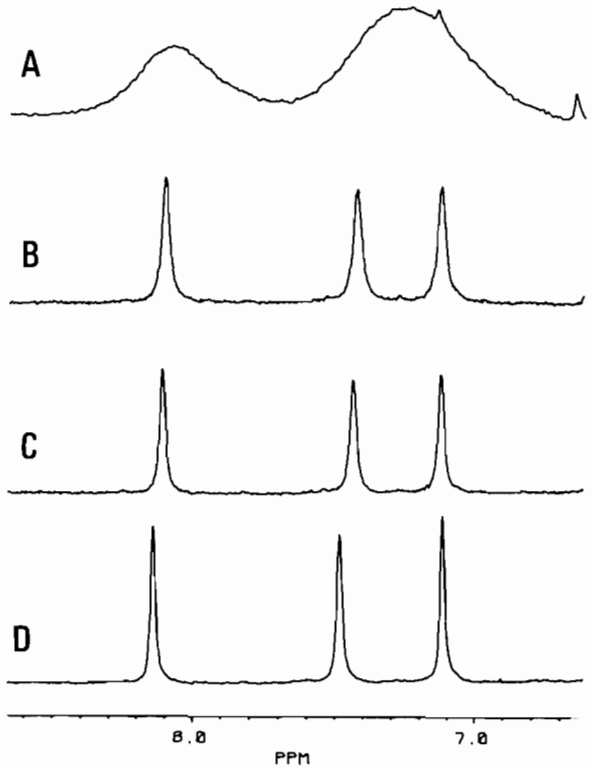

Fig. 4. Evolution of the ^1H NMR spectrum of ImH with temperature in $[(AE)NiImH]^+$; A, 323; B, 263; C, 253; D, 223 K.

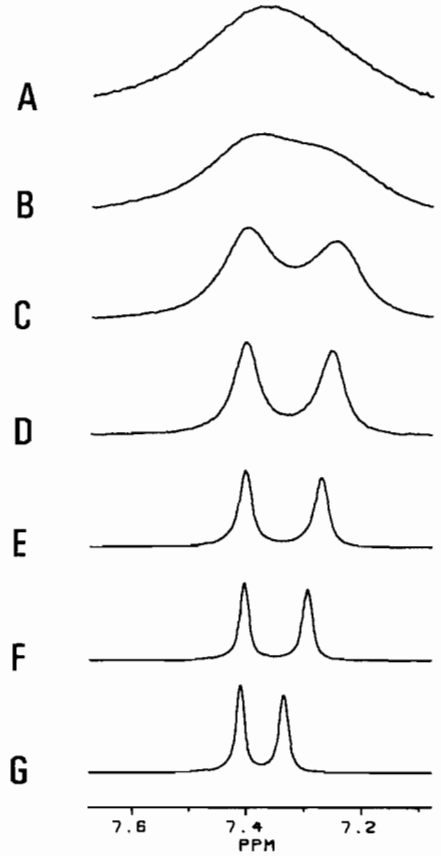

Fig. 5. ^1H NMR of $[(AE)Ni2\text{-}MeImH]^+$. Signals of 2-MeImH at different temperatures: A, 323; B, 313; C, 294; D, 273; E, 253; F, 233; G, 203 K.

60 Hz). Below 325 K the spectrum decoalesces and the signal widths decrease: $\Delta\nu_{1/2} = 16.7$, 6.0 and 3.5 Hz at 295, 275 and 205 K respectively. Surprisingly the signals separation remains constant ($\Delta\delta = 0.15$ ppm) from 295 K to 263 K and then decreases ($\Delta\delta \approx 0.07$ ppm at 203 K). During this second step the H(5) resonance is practically not affected while the H(4) is deshielded by *ca.* −0.10 ppm. This is to be compared with the behaviour of H(4) in **3** and **4** where an upfield shield is observed on lowering the temperature. Similarly the imidazole CH_3 signal of **6a** is significantly deshielded ($\Delta\delta$ = −0.5 ppm) on going from 295 to 205 K while the CH_3 signal of the 5-MeIm isomer **6b** is marginally affected (+0.05 ppm).

Finally it is obvious that tautomerism cannot justify alone all these data. It is likely that an alteration of the quadrupolar relaxation may be partly responsible for the narrowing of the resonance lines at low temperatures. However, this explanation cannot account for the shielding and deshielding effects. As suggested by the ^{13}C spectra these effects could originate in a conformational process. This point will be considered later.

Discussion

From the data quoted in Table I it appears that the ^{13}C shifts of the AE moiety are insensitive to the nature of the second ligand. As previously noted this is not the case for the ^1H shifts since the shifts of methyl group ($OCCH_3$) and, to a smaller extent, of the NH_2 group take different values according to the position of the methyl substituent on the imidazole ring:

$-\delta(OCCH_3) = 1.73 \pm 0.03$ ppm and $\delta(NH_2) = 3.4 \pm 0.1$ ppm in the complexes involving 2-MeImH, 4-MeImH, BzImH, 2-MeIm$^-$, 4-MeIm$^-$ and BzIm$^-$;

$-\delta(OCCH_3) = 1.85 \pm 0.02$ ppm and $\delta(NH_2) = 3.7 \pm 0.1$ ppm in the complexes involving ImH, 1-MeIm, 5-MeImH and Im$^-$.

Regarding the imidazole moiety, the significant parameter seems to be the complexation shift, *i.e.* $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$ (*cf.* Table IV). In all the mononuclear complexes, low-temperature data point to deshielding of H(2) and H(5) while H(4) is either shielded or deshielded. These effects are very similar to those previously observed for cobalt complexes

[2, 8 and refs. therein] and may be essentially attributed to the influence of σ-charge donation to the metal. A point of interest results from the observation that the CH_3 resonance is much more affected by complexation in 2- and 4-MeImH ($\Delta\delta$ = 0.60 and 0.53 ppm respectively) than in 1- and 5-MeImH ($\Delta\delta$ = 0.10 and −0.02 ppm respectively).

Finally these data emphasize the importance of the methyl substituent at positions 2 and 4 of ImH with regard not only to the resonances of imidazole but also to (AE). This suggests, as did the ^{13}C data previously, that we are faced with a conformational problem.

Molecular models and available structural data [1] point to possible steric interactions between, on the one hand, the OC*CH*$_3$ and *NH*$_2$ groups of AE and, on the other hand, a *CH*$_3$ substituent at the 2 or 4 positions of the imidazole ring. These non-bonded interactions are expected to cause either an increase of the angle of the Ni–N(3) and N(3)–C(2) vectors or a twist of the dihedral angle formed by the equatorial coordination plane and the imidazole plane. The first situation has been observed in a cobalt complex of the 1,2-dimethylimidazole [13] for which structural studies have shown that the 2-methyl substituent causes a 'tilt' of the imidazole bond which places H(4) closer to the metal than in the corresponding non-substituted ImH complex [14]. Numerous examples of the second deformation are known [1, 8, 15–20]. They suggest that non-substituted imidazole would not display important steric requirements on its own. However tendency towards a preferred orientation could be caused by introduction of a methyl substituent at a position (2 or/and 4) adjacent to the nitrogen donor and steric interaction of this substituent with a second ligand in the coordination sphere of the metal. This would offer a rationale to the behaviour of the complexes of the present study. Indeed modification of the orientation of the imidazole ring with respect to the coordination plane under the influence of non-bonded interactions would cause a change in the magnitude and even in the sign of the effects exerted by the magnetic anisotropy of the imidazole ring upon the protons of (AE). It may be recalled that the spectral (^1H, ^{13}C) modifications caused by varying the temperature are fully consistent with the existence of preferred conformations.

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