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# New Route to Bimetallic Imidazolate-bridged Complexes.
# III. Solution Properties of Dinuclear Copper and Nickel Complexes and their Mononuclear Precursors

J.-P. COSTES* and J.-P. LAURENT

*Laboratoire de Chimie de Coordination du CNRS, Unité no. 8241 liée par convention à l'Université Paul Sabatier, 205 route de Narbonne, 31077 Toulouse Cédex, France*

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## Abstract

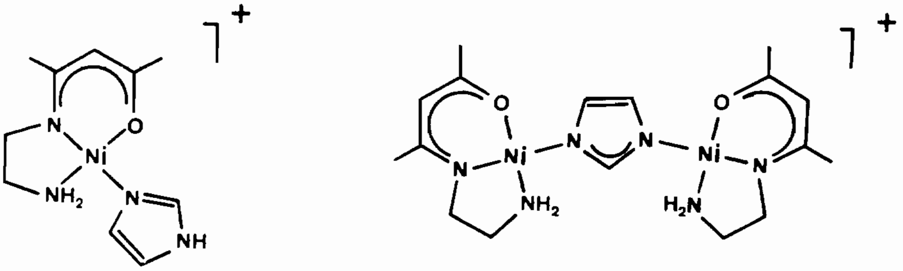
Solution study of the dinuclear imidazolate-bridged complexes shows that the dimeric structure is retained even in good coordinating solvents such as pyridine, DMSO or imidazole. The mononuclear nickel complex which is diamagnetic in the solid state and in non-coordinating solvents becomes fully paramagnetic in the presence of an excess of pyridine. Its homodinuclear homologue displays a rather different behaviour for addition of pyridine gives rise to a limited paramagnetism seemingly corresponding to one nickel ion on two becoming high-spin. A similar behaviour characterizes the heterodinuclear complex. EPR spectra of the dicopper complexes emphasize the importance of dipolar interactions in the solid state and in non-coordinating solvents. However they are removed by good donor solvents.

## Introduction

We have previously reported the synthesis and solid-state properties of a dicopper imidazolate-bridged complex and its heterodinuclear (Cu, Ni) homologue which has been structurally characterized [1]. The present paper is devoted to the solution properties (electronic spectra, static magnetic susceptibilities and EPR spectra) of these complexes and their mononuclear precursors (Fig. 1). Because of their relatively simple structure, these species are expected to allow a comparative description of the behaviour of the imidazole and imidazolate ligands. This may be of interest due to the frequent occurrence of imidazole derivatives in biologically important complexes.

## Experimental

The ligand 7-amino-4-methyl-5-aza-3-hepten-2-one [2], abbreviated AEH in the following and AE when deprotonated, and the different complexes used in this study were synthesized according to literature procedures described earlier [1, 3]. The only new compound is $[(AE)NiPyraNi(AE)](ClO_4)_2$. The preparation is similar to that of $[(AE)NiPy](ClO_4)$ [4] by substitution of pyridine for pyrazine. The abbreviations ImH, $Im^-$, Py and Pyra stand for imidazole, imidazolate, pyridine and pyrazine. For



M = Ni, $[(AE)NiImH]^+$ (**Ia**)
M = Cu, $[(AE)CuImH]^+$ (**Ib**)

M = M′ = Ni, $[(AE)NiImNi(AE)]^+$ (**IIa**)
M = M′ = Cu, $[(AE)CuImCu(AE)]^+$ (**IIb**)
M = Ni, M′ = Cu, $[(AE)NiImCu(AE)]^+$ (**IIab**)

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

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*Author to whom correspondence should be addressed.

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the sake of simplification, the different complexes are substituted by numbers in the text, as indicated in Fig. 1.

Visible spectra were recorded using a Cary 2390 spectrophotometer. EPR spectra were obtained with a Bruker 200 TT spectrometer in the X-band region at 9.4 GHz on samples prepared as solids, as liquids at ambient temperature or as glasses at 110 K in round quartz sample tubes. Magnetic susceptibility measurements of these complexes in solution were determined by nuclear magnetic resonance [5] using pyridine as solvent and t-butanol as indicator.

## Results

### *Electronic Spectroscopy*

The data reporte in Table I reveal that the spectra of all the complexes under investigation are solvent-dependent. As expected, spectra of acetone solutions are almost identical with Nujol mull spectra whereas in potentially coordinating solvents, methanol, pyridine, their overall appearance is modified.

TABLE I. Electronic Spectra (nm) with Absorption Coefficients in Parentheses

| Compounds | Acetone | Pyridine |
|---|---|---|
| **Ia** | 455(300) | 545(15)<br>775(11)<br>830(13) |
| **IIa** | 455(400) | 435(230)<br>775(10)<br>830(13) |
| **Ib**[a] | 560(110) | 595(115) |
| **IIb** | 570(280) | 600(220) |
| **IIab** | 450(240)<br>560(90) | 435(200)<br>590(110) |

[a]DMSO: 600 nm; MeOH: 580 nm.

The modifications are particularly significant in the case of the nickel complexes. In inert solvents, the mononuclear and dinuclear nickel complexes give the same spectral pattern with an absorption at 455 nm which is attributable to a $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition. This location is characteristic of a square-planar geometry and a relatively strong ligand field. Methanol solutions of the monomeric species **Ia** show not only the absorption at 455 nm but also two supplementary bands of low intensity at 535 and 830 nm. These absorptions are also clearly present in the spectra of pyridine solutions but the 460 nm band is no longer observed. These data point to the simultaneous presence of two forms in methanol, the square-planar form previously observed in inert solvents and a pseudo octahedral form resulting from apical coordination of solvent molecules, the latter species being exclusively present in pyridine. In the dinuclear complex **IIa**, the absorption at 455 nm does not vanish in pyridine but is shifted to 435 nm while the bands characteristic of the octahedral form are observed at 775 and 830 nm. This behaviour has to be compared to that of the heterodinuclear complex **IIab** whose spectra in pyridine show bands at 590 and 430 nm, attributable to a penta- or hexacoordinated copper ion (*vide infra*) and a nickel ion in square-planar geometry. The absorptions characteristic of a nickel ion in an octahedral environment at *ca.* 550 and 830 nm are not observed. It appears that the propensity of the nickel ion for enlarging its coordination number decreases in going from the mononuclear to the homo- and heterodinuclear complexes.

For the copper complexes, the d–d transitions apparently all occur under a broad envelope with a maximum at 560 nm in Nujol mull and acetone solution spectra. This position is consistent with a planar or weakly tetragonal geometry. Replacing the inert solvent acetone by pyridine moves the maximum to 600 nm. This shift supports an enlargement of the coordination number of the copper ion to five or six. At this point, the two possibilities cannot be differentiated since according to Hathaway [6] they are expected to give very similar ligand-field spectra.

It may be noted that the square-planar complexes under investigation display an absorption located at lower wavelengths than usually observed for the nickel and copper complexes of similar tetradentate Schiff bases ligands with orthophenylenediamine as diamine bridge. Indeed for these complexes the maximum occurs in the range 550–630 and 620–650 nm, respectively [7].

### *Magnetic Properties*

The mononuclear and dinuclear nickel complexes are diamagnetic in the solid state and in non-coordinating solvents. Solutions in pyridine display a paramagnetic behaviour. Room temperature measurements (Evan's method) yield an effective magnetic moment per molecular unit of 3.0 BM in both cases (**Ia** and **IIa**). Thus the mononuclear complex becomes fully paramagnetic whereas the propensity towards high-spin state is actually limited in the dinuclear complex. In the latter instance, the observed moment has the value expected for one nickel contributing to the paramagnetism of the dinuclear unit. An almost identical value of 3.0 BM is obtained when pyridine is replaced by imidazole. Furthermore, practically identical values of the moment characterize a solid sample of the heterodinuclear complex ($\mu$ = 1.8 BM) and a solution in pyridine ($\mu$ = 1.9 BM). These observations suggest that in the limiting case of a large excess of donor (pyridine, imidazole), the nickel atom in **IIab** remains four-coordinated as does one of the two nickel atoms in **IIa**.

Magnetic susceptibility data were collected for solid samples of **Ib**, **IIb** and **IIab**. The heterodinuclear complex (**IIab**) follows a Curie-Weiss law, $\chi_M^{corr} = C/(T - \theta)$ where $C = 0.38$ deg cm$^3$ mol$^{-1}$ and $\theta = -0.4 \pm 0.2$ K. From the non-zero value of $\theta$, intermolecular interactions have been inferred. An antiferromagnetic coupling ($2J = -43.0$ cm$^{-1}$) has been evidenced in the case of the dicopper complex [1].

ESR spectra related to powdered samples of the dinuclear complexes **IIb** and **IIab** have been previously reported [1]. The corresponding data are recalled in Table II together with the results obtained for solutions in various solvents of **Ib**, **IIb** and **IIab**.

Whereas the solid state spectrum of **Ib** is devoid of any hyperfine structure, coupling to the copper nucleus is clearly seen on the parallel component ($g_\parallel \sim 2.2$) of solution spectra. In addition for MeOH and DMSO solutions, seven hyperfine lines ($|A_N| = 13$ G) are observed on the perpendicular signal ($g_\perp \sim 2.05$) in accordance with the occurrence of three nitrogen donors in the coordination sphere. Interestingly, the $g$ and $A$ values are solvent-dependent. The presence of a potential donor, *i.e.* MeOH, DMSO, Py and ImH, causes an increase of the $g$ values and a decrease of the $|A|$ values. These effects are likely due to axial ligation of solvent molecules [8, 9]. Interestingly, successive additions of imidazole to a methanolic solution of **Ib** reduce markedly the magnitude of $|A_\parallel(\mathrm{Cu})|$ but do not modify the number of N-superhyperfine lines. Even with a large excess of ImH, seven lines are observed. According to the conclusions of a recent study [10], this would be in line with the formation of a diadduct [(AE)Cu(ImH)$_3$]$^+$ with four strong in-plane bonds and two weaker axial bonds. Indeed in a monoadduct [(AE)Cu(ImH)$_2$]$^+$ the five bonds would become more similar in magnitude through an out-of-plane bending of the equatorial bonds. In this instance, nine N-shf lines would be observed since the presence of aromatic N donors is expected to cause an activation of the system in such a way that all N donors would exhibit equivalent contributions to the N-shf structure.

TABLE II. EPR Data

| | $g_{iso}$ [a] | $A_{iso}$ [a, c] | $g_\parallel$ [b] | $g_\perp$ [b] | $A_\parallel$ [b, c] |
|---|---|---|---|---|---|
| **Ib** | | | | | |
| Solid | | | 2.175 | 2.06 | |
| Acetone | 2.100 | 86 | | | |
| MeOH | 2.104 | 83 | 2.219 | 2.05 | 189 |
| Pyridine | 2.111 | 78 | 2.223 | 2.05 | 187 |
| DMSO | | | 2.220 | 2.05 | 188 |
| (MeOH + 2ImH) | 2.104 | 83 | 2.215 | 2.05 | 190 |
| (MeOH + *n*ImH) | | | 2.235 | 2.05 | 177 |
| **IIb** | | | | | |
| Solid | | | 2.08 | | |
| Acetone, MeOH | | | 2.08 | | |
| Pyridine | 2.109 | 79 | 2.216 | 2.05 | 183 |
| DMSO | | | 2.217 | 2.05 | 192 |
| **IIab** | | | | | |
| Solid | | | 2.08 | | |
| Acetone | | | 2.186 | 2.07 | 185 |
| MeOH | 2.103 | 83 | 2.213 | 2.05 | 189 |
| Pyridine | 2.108 | 77 | 2.229 | 2.05 | 176 |
| DMSO | | | 2.215 | 2.05 | 190 |

[a] Ambient temperature. [b] 110 K. [c] $A$ in Gauss.

Pure solid samples of the homo- and heterodinuclear complexes **IIb** and **IIab** give similar spectra with a broad intense signal at $g \sim 2.08$ and a much weaker signal at $g \sim 4.3$. The latter feature which is attributable to a $\Delta M = 2$ transition disappears when the complexes are diluted in their diamagnetic homologue **IIa**, whereas the two components of the $\Delta M = 1$ transition become clearly separated in the case of **IIab**. Diluted samples of the dicopper complex **IIb** yield spectra characterized by a broad absorption centered at $g \sim 2.08$. Very similar features, *i.e.* an axial spectrum for **IIab** and one broad signal for **IIb**, are observed for frozen solutions spectra in non-coordinating solvents. The use of potentially coordinating solvents (Py, DMSO) results in axial spectra for both complexes. From these data it may be inferred that interactions between the individual dinuclear units are operative in solid samples and they are mainly dipolar in character. As expected, they are no longer observed when diluted samples of **IIab** are studied. Surprisingly for the dicopper complex **IIb**, diluted samples in non-coordinating solvents seemingly give one broad $\Delta M = 1$ transition suggesting that some type of interaction is still operative. However, it is not clear whether the spectrum actually displays one signal or two signals. In this last instance, the parallel component of intrinsic low intensity would be masked by the perpendicular component. In the former case, the quasi-isotropic spectrum would result from intramolecular exchange interaction whereas in the latter case the broadening of the main signal would be due to intermolecular interaction of the dipolar type. One may think that the modifications caused by the change of solvent from an inert one to a coordinating one have to be related to breaking of the imidazole bridge. This is probably not the case. Indeed solutions of **Ib** and **IIb** in methanol and dimethylsulphoxide display almost identical conductibilities, the obtained values ($\Lambda = 80 \pm 5$ $\Omega^{-1}$ m$^2$ eq$^{-1}$ in MeOH and $30 \pm 3$ $\Omega^{-1}$ m$^2$ eq$^{-1}$ in DMSO) being consistent with 1:1 electrolytes. Furthermore, NMR ($^1$H and $^{13}$C) spectra of the dinickel complex **IIa** in DMSO and in mixed solvents (MeOH + Py) obviously support a dinuclear structure with an imidazole bridge since, in both cases, the equivalence of the C(4)H and C(5)H groups of imidazole is retained [3].

## Discussion

As previously noted, in a given solvent the three complexes **Ib**, **IIb** and **IIab** display almost identical copper d–d spectra. This suggests that replacing ImH by $Im^-$ and even by the pseudo-ligand $Im^-Ni(AE)$ does not cause any significant change in the ligand field experienced by the copper ion. However, the ligand field is modified when an inert solvent, acetone, is replaced by a potentially coordinating one, pyridine or ImH. As expected on the basis of a simple ligand-field splitting diagram [9] the absorption is shifted from *ca.* 560 nm (17 900 $cm^{-1}$) to 590 nm (16 800 $cm^{-1}$) in relation with a lowering of the interactions between the metal and the equatorial ligands. The influence of the coordinating solvent is also perceptible in the EPR spectra, giving rise to a decrease of $|A_{iso}|$ and to an increase of $g_{\parallel}$.

The mononuclear complex **Ia** does not present any particular point but the behaviour of the homo- and heterodinuclear complexes deserve further comments in connection with the fact that the possibility of coordinating pyridine is seemingly restricted to one metal ion. Steric hindrance is not a likely explanation since in $[(AE)NiPyraNi(AE)]^{2+}$ which is expected to show similar steric requirements, both nickel ions become high-spin in the presence of pyridine. A possible explanation is suggested by the generally accepted view that imidazolate exerts a greater ligand field than neutral imidazole. However, it may be recognized that the increase in ligand field strength is not perceptible in the electronic spectra since the maximum occurs at the same wavelength in **Ia** and **IIa**. Furthermore, the presence of the imidazolate ligand in the latter complex does not completely prevent axial coordination of solvent molecules (Py, ImH) since in the presence of a large excess of solvent, the dinuclear unit has a magnetic moment of 3.0 BM. We feel that the main effect originates precisely in the coordination of pyridine to the first metal ion, resulting in a pseudo-ligand $[Im^-M(Py)_2(AE)]$ which would exert an increased field upon the second metal ($Ni_B$) ion. Indeed, axial coordination of pyridine to M is expected to lower the interaction between the metal and the equatorial ligands, resulting in a destabilization of rhe related orbitals and, more particularly, the orbitals of $\sigma$-symmetry of the imidazolate. This would favour the interactions of this $Im^-$ ligand with the second nickel ion ($Ni_B$) whose $d_{x^2-y^2}$ orbital would be raised in energy to a sufficient extent to prevent spin-unpairing. This oversimplified description implies that a significant modification of the ($Ni_B$) spectrum would be induced by coordinating pyridine on the first metal ion M. This is actually observed with a shift of the ligand field maximum from 455 nm (21 980 $cm^{-1}$) to 435 nm (22 990 $cm^{-1}$).

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