

ACID IONIZATION CONSTANTS OF COORDINATED LIGANDS

M. J. CALHORDA
A. R. DIAS⁽¹⁾

Centro de Química Estrutura
Complexo I
Instituto Superior Técnico
Lisboa — Portugal

Deprotonation reactions of coordinated ligands have received some attention as part of general studies on the reactivity of chelated organic ligands [1]. Particular emphasis has been placed on the deprotonation studies of coordinated imidazole derivatives [2, 6] partly on the grounds of the biological significance of these ligands [6, 7].

In the present note we wish to report our preliminary results on the deprotonation studies of the imidazole derivatives and related ligands given in the figure when these are coordinated to the $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}$ moiety.

Complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{HL-L}')](\text{PF}_6)_2$, where $\text{M} = \text{Mo}, \text{W}$ and $\text{HL-L}'$ represents ligands I to VI, were isolated and fully characterized. These are, to our knowledge, the first complexes reported of these ligands with Mo or W. The acid ionization constants of the coordinated ligands were determined by potentiometric titration of the complexes in acetone/water (1:1) with an aqueous solution of KOH; the pK_a values obtained are given in the table. The deprotonated species were also isolated and characterized by analytical and spectroscopic techniques.

In agreement with the published data a general increase in the acidity of the ligands upon coordination was observed. This has been taken to show that the electronic shift which occurs as a consequence of metal-nitrogen (and, to some extent, metal-oxygen) bond formation can be transmitted through the aromatic ring decreasing the electron availability at the imino nitrogen and facilitating the deprotonation reaction [1].

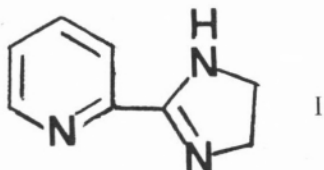
The relative acidities of the various coordinated ligands, as measured by the pK_a values, follow the extent of delocalization of the π -electron density of the ligands and reflected the withdrawing and pushing properties of the nitrogen and oxygen donor atoms respectively. As expected, the increase in acidity upon coordination is maximal for ligands III and IV and negligible for ligand V.

It has been suggested that the increase in acidity of the imino hydrogen of the imidazole or imidazoline nucleus is a function of the metal-nitrogen bond strength [3]. On these grounds our observation of a consistently higher acidity of the tungsten complexes seems to indicate the following order for the bond strengths: $\text{W-N} >$

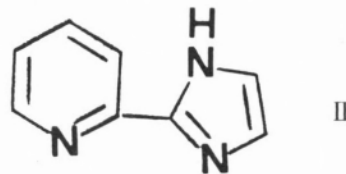
(1) —Author to whom correspondence should be addressed.

$>Mo-H.N.$ That suggestion has been questioned recently [7]. Future thermochemical studies may provide the necessary evidence to establish this point more firmly.

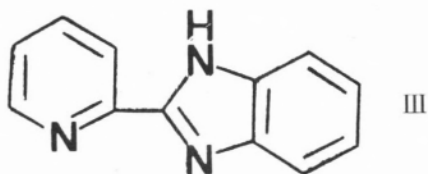
Studies to extend the work described here to analogous complexes with different metals, namely Ti (III) and Nb (IV) are now under way.



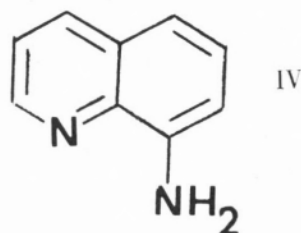
2-(2'-pyridyl) imidazoline
(Hpyim)



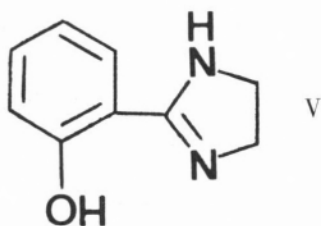
2-(2'-pyridyl) imidazole
(Hpym)



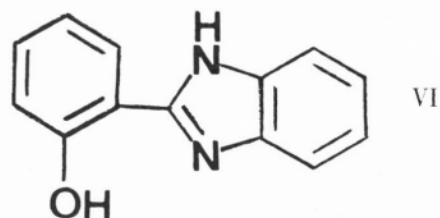
2-(2'-pyridyl) benzimidazole
(Hpyb)



8-aminoquinoline
(Hamq)

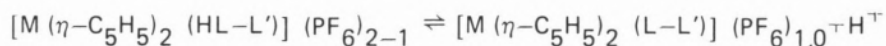


2-(o-hydroxyphenyl) imidazoline
(Hhpim)



2-(o-hydroxyphenyl) benzimidazole
(Hhpb)

Table
Acid Ionization Constants



Complex	pK_a^a	Complex	pK_a^a
$[Mo(\eta-C_5H_5)_2(Hpyim)](PF_6)_2$	$\sim 9.9^b$	$[W(\eta-C_5H_5)_2(Hpyim)](PF_6)_2$	9.12 ± 0.03
$[Mo(\eta-C_5H_5)_2(Hpym)](PF_6)_2$	5.20 ± 0.03^c	$[W(\eta-C_5H_5)_2(Hpym)](PF_6)_2$	4.68 ± 0.03^c
$[Mo(\eta-C_5H_5)_2(Hpyb)](PF_6)_2$	3.98 ± 0.03	$[W(\eta-C_5H_5)_2(Hpyb)](PF_6)_2$	3.53 ± 0.03
$[Mo(\eta-C_5H_5)_2(Hamq)](PF_6)_2$	4.08 ± 0.03	$[W(\eta-C_5H_5)_2(Hamq)](PF_6)_2$	3.14 ± 0.03
$[Mo(\eta-C_5H_5)_2(Hhpim)]PF_6$	$\sim 11-12^b$	$[W(\eta-C_5H_5)_2(Hhpim)]PF_6$	$\sim 11-12^b$
$[Mo(\eta-C_5H_5)_2(Hhpb)]PF_6$	8.40 ± 0.03	$[W(\eta-C_5H_5)_2(Hhpb)]PF_6$	8.03 ± 0.03

a — $0.03 = \sigma_m \cdot t$ where σ_m is the mean standard deviation and t is the Student parameter for 95 % probability and between 6 and 8 degrees of freedom. Calculations were made using the method reported by SILVA [8].

b — Values not very reliable because the acid is very weak and the pH values were measured in a region where the electrode gives a large error.

c — For the free ligand $pK_a = 14.2 \pm 0.2$ in ethanol/water (13.4 ± 0.1 in water) [7].

For the other free ligands no pK_a values have been reported for the acid dissociation of the nitrogen bonded hydrogen of the neutral ligand.

Received 30 June 1978

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