Laser Induced Vaporization Mass Spectrometry of a High Melting Multidentate Chelating Ligand and its Ni(II) Bisdeprotonated Complex

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Abstract

The laser induced vaporization of 2,6-diacetylpyridine-bis(1-phthalazinylhydrazone) and of bis[2,6-diacetylpyridine-bis(1-phthalazinylhydrazonato)nickel-(II)] allowed an easy description of the Electron Impact (EI) induced fragmentation pattern of the two compounds. The comparison with the spectra obtained with the usual heated probe is reported, showing that in that case the mass spectra collected are due to pyrolysis products.

Introduction

Mass spectrometry has been always widely employed in the field of coordination compounds mainly due to the structural information power of this technique [1]. In the last few years, the development of new ionization techniques, alternative to the usual Electron Impact (EI) one, allowed the mass spectrometry studies to be extended to classes of compounds labile thermally and/or to electron impact [2].

In most cases, the problem arises from the volatilization of the sample: using the commonly available direct insertion probes, coordination compounds often undergo thermal decomposition before or during volatilization, so that the resulting mass spectra are, in the best case, the overlapping of the spectra due to the sample itself and its pyrolysis products. This is the main reason why coordination chemists look critically at mass spectrometric data.

Since 1980 we have successfully experimented on the best sample evaporation conditions, in order to avoid these pyrolysis phenomena, and described a simple method (direct electron impact) [3] which consists of a molecular distillation of the sample into the ion source of the mass spectrometer. More recently we have shown the possibility of a simple coupling of the mass spectrometer with a laser, by means of an optic fiber mounted in a hollow probe [4]. By means of such an arrangement all the instrumental devices necessary in laser desorption experiments [5] (microscope, modifying of the ion source housing, pilot laser etc.) are avoided.

In the present paper we report the comparative, laser induced vaporization EI mass spectrometry of 2,6-diacetylpyridine-bis(1-phthalazinylhydrazone) ([H_2L] compound **1**) and of bis[2,6-diacetylpyridine-bis(1-phthalazinylhydrazonato)nickel(II)] ([LNi]$_2$ compound **2**) [6] whose melting points are higher than 300 °C.

Experimental

All mass spectrometric measurements were performed on a VG ZAB 2F instrument operating in EI conditions (70 eV, 200 μA). Metastable transitions were detected by B/E linked scans [7]. The laser vaporization of the sample was obtained by coupling the laser and the sample into the ion source through an optic fiber [8] mounted into a hollow probe as already described by us [4].

The ruby rod is 10 cm long and with a diameter of 6.3 mm. It is pumped by two linear Xe flash lamps (ED SG, mod. 7FX-4, max. average power 3850 W) in a double elliptical cavity. The optical resonator consists of a flat 60% deflecting mirror and of a 100% reflecting mirror with a curvature radius of 5 mt. The maximum output energy is about 4 J. The output beam is focalized on the fiber by means of a lens of 300 mm focal length.

All the measurements reported in this paper have been obtained with an output energy from the fiber of about 0.5 J. Compounds **1** and **2** were analytically pure samples synthesized and purified according to the literature [6].

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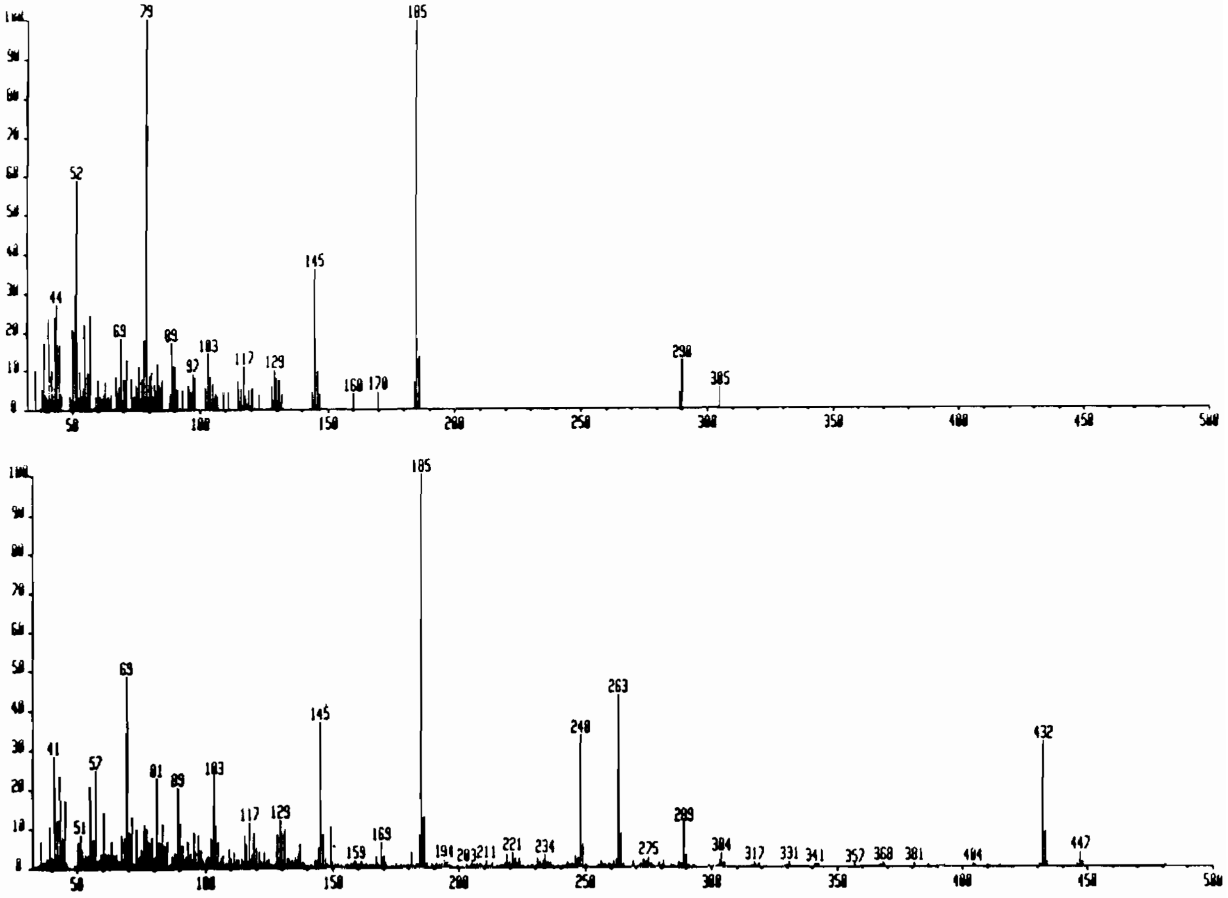


Fig. 1. The 70 eV EI mass spectra of the ligand H_2L (**1**): in the upper part as obtained by heating the sample at 350 °C by the direct inlet probe, while in the lower part as obtained by laser induced vaporization of the sample.

Results and Discussion

In the upper part of Fig. 1, the 70 eV EI mass spectrum of compound **1**, as obtained by heating the sample by the direct inlet probe at 350 °C is reported, while in the lower part of the same figure the 70 eV EI mass spectrum of **1** as obtained by laser induced vaporization of the sample is shown.

The potentially of the latter technique is evident at first sight: well detectable molecular ions are present at *m/z* 447 and most of the peaks are due to ionic species well related to the original structure.

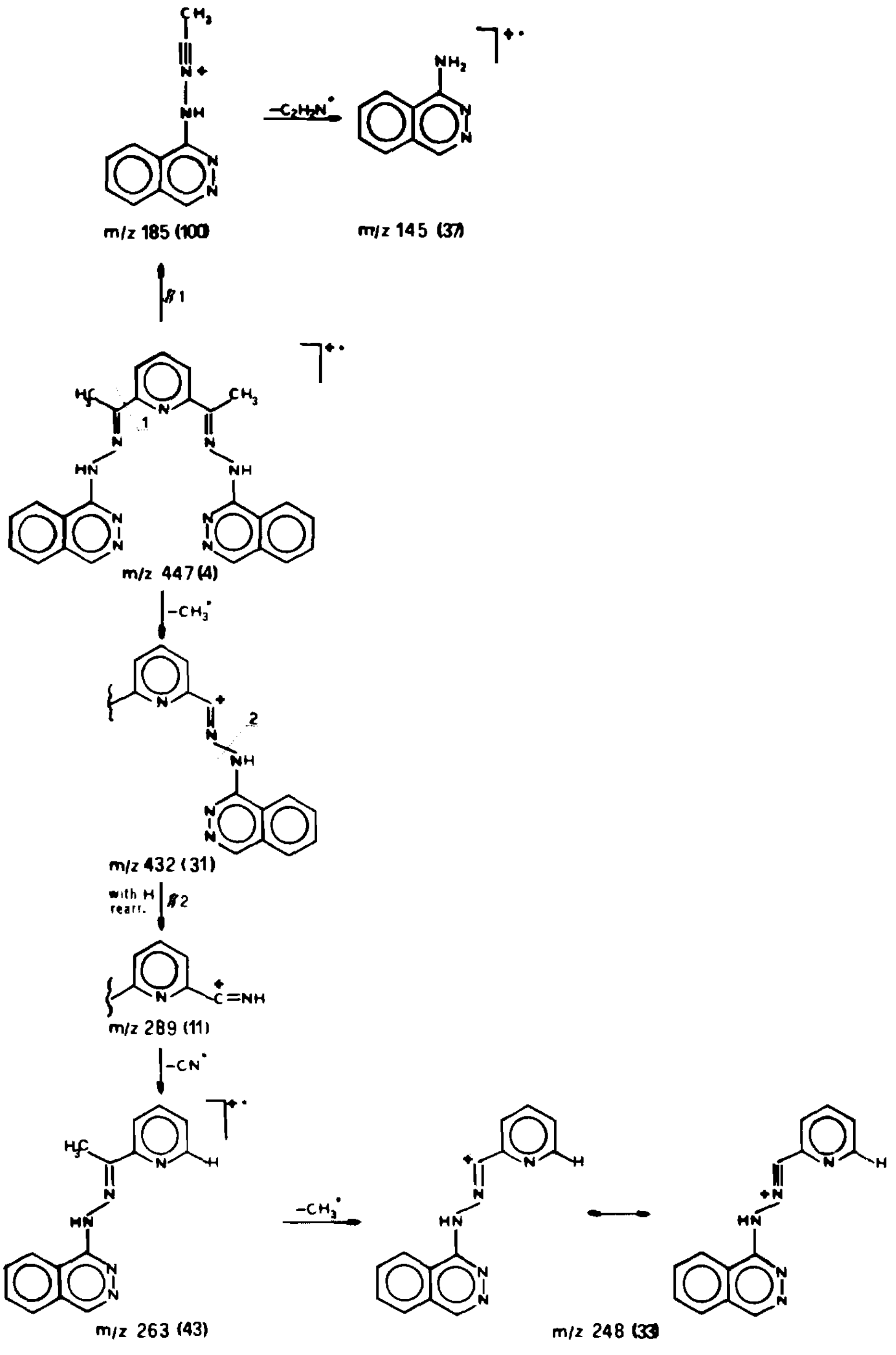
By means of B/E linked scans, the fragmentation pattern reported in Scheme 1 has been obtained. The primary methyl loss is responsible for the formation of the abundant ionic species at *m/z* 432, while the cleavage of the C–C bond in the side chain in position 2 of the pyridine leads to the ionic species at *m/z* 185, which represents the base peak of the spectrum.

The cleavage of the N–N bond in the ions at *m/z* 432 gives rise to the ionic species at *m/z* 289, probably bearing an imino group in position 2 of the pyridine. Further $CN^{\bullet}$ and $CH_3^{\bullet}$ losses lead to the even electron ion at *m/z* 248, for which two different resonating formulae can be invoked. Ions at *m/z* 145 originate from the ionic species at *m/z* 185 through a $C_2H_2N^{\bullet}$ loss, leading to 1-amino-phthalazine molecular ion.

On the contrary, the usual EI spectrum (see upper part of Fig. 1) does not show any molecular ion. The higher mass peak is at *m/z* 305, probably due to the pyrolysis of **1**. For these ionic species the structure of a 2-formyl-hydrazone derivative can be reasonably proposed, looking either at the presence of their complementary species at *m/z* 130 or at their fragmentation patterns (see Scheme 2).

The only primary decomposition pathways of ionic species at *m/z* 305 are due to methyl loss (leading to ions at *m/z* 290) and to the cleavage of the C–C bond already described, giving rise to two complementary ionic species at *m/z* 185 and 120.

In the same spectrum the presence of abundant ionic species at *m/z* 79, corresponding to the pyridine molecular ion suggests the presence of other thermally induced decomposition pathways.

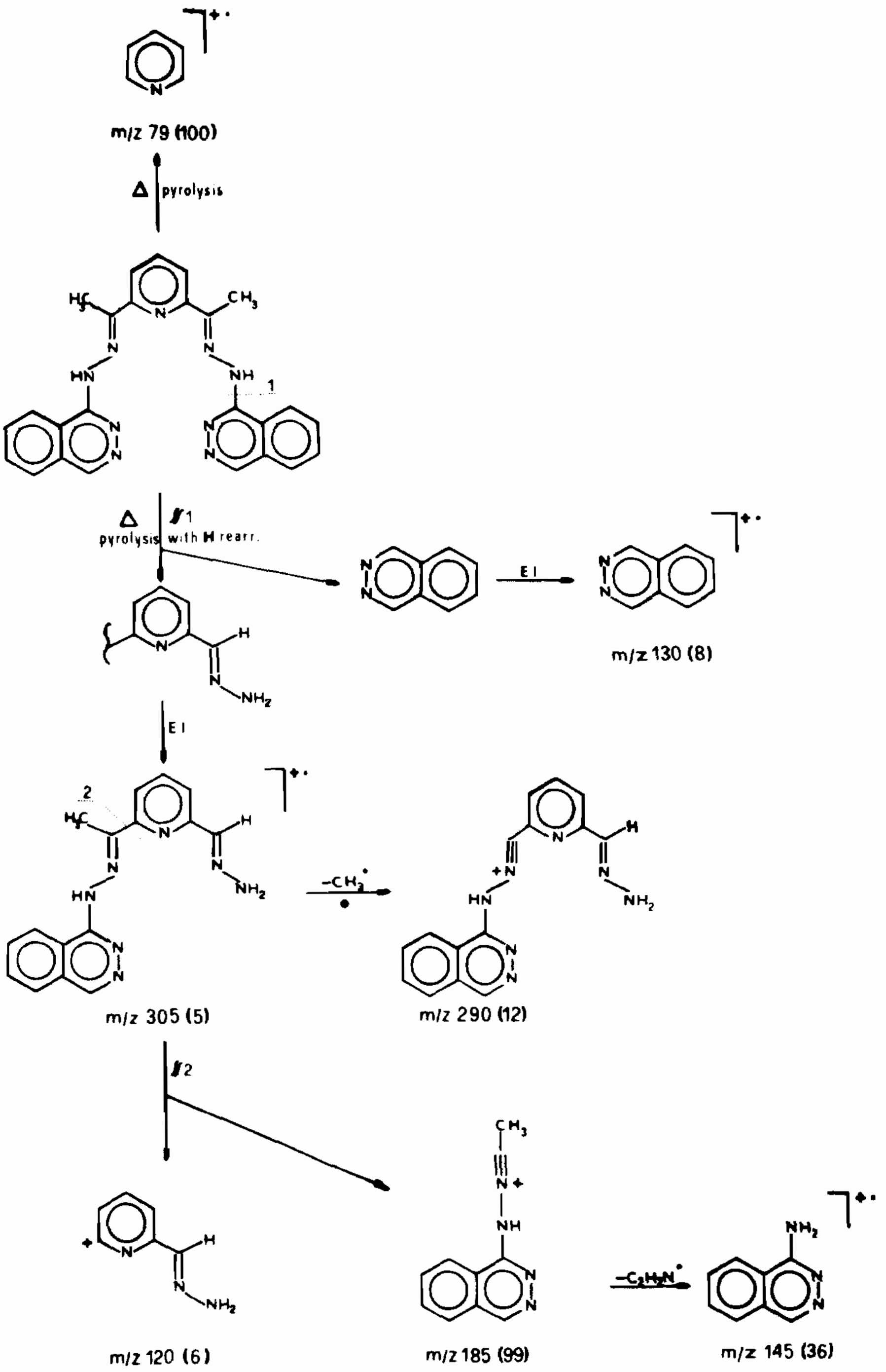


Scheme 1.

As far as the mass spectrometric behaviour of $[LNi]_2$ (2) is concerned, it is noteworthy that also in this case the laser induced vaporization technique reveals its peculiarities (see Fig. 2).

In fact, while under the usual EI conditions (by using the heatable–coolable direct insertion probe), neither molecular ions nor abundant nickel-containing ionic species are ever detected, under laser induced vaporization conditions several interesting features have been observed (see Scheme 3).

(i) The presence of molecular ions at *m/z* 1006, which confirms the dimeric nature of complex 2, as observed in solid state [6], and accounts for its stability in both the gas phase and the ionic state.



Scheme 2.

(ii) The presence of several fragment ions containing two Ni atoms contemporary bonded to one unmodified ligand and to different residual groups coming from cleavages of the second ligand molecule (ions b, c, and further fragmentation products).

(iii) The base peak is due to an organic species at *m/z* 368 (ion d of Scheme 3). For such ions the structure of 5,6-diphthalazinyl-4,5-dimethyl-1,4,5,6-tetraazacyclohexa-1,3-diene could be reasonably proposed in agreement with its further fragmentation processes. In particular the most favourable fragmentation process leading from d ions at *m/z* 256 can be explained by the condensation of the two phthalazinyl moieties and the formation of highly

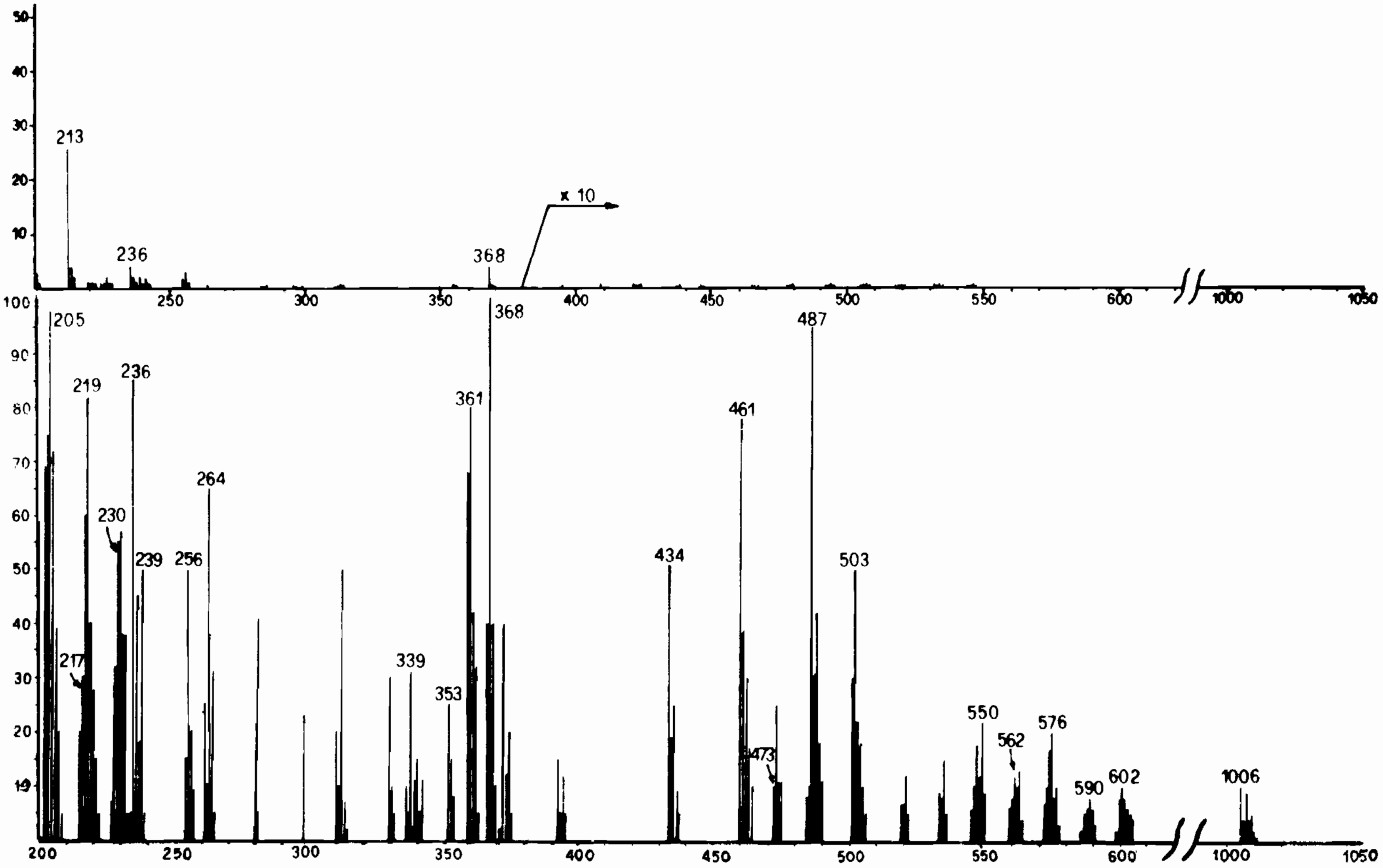
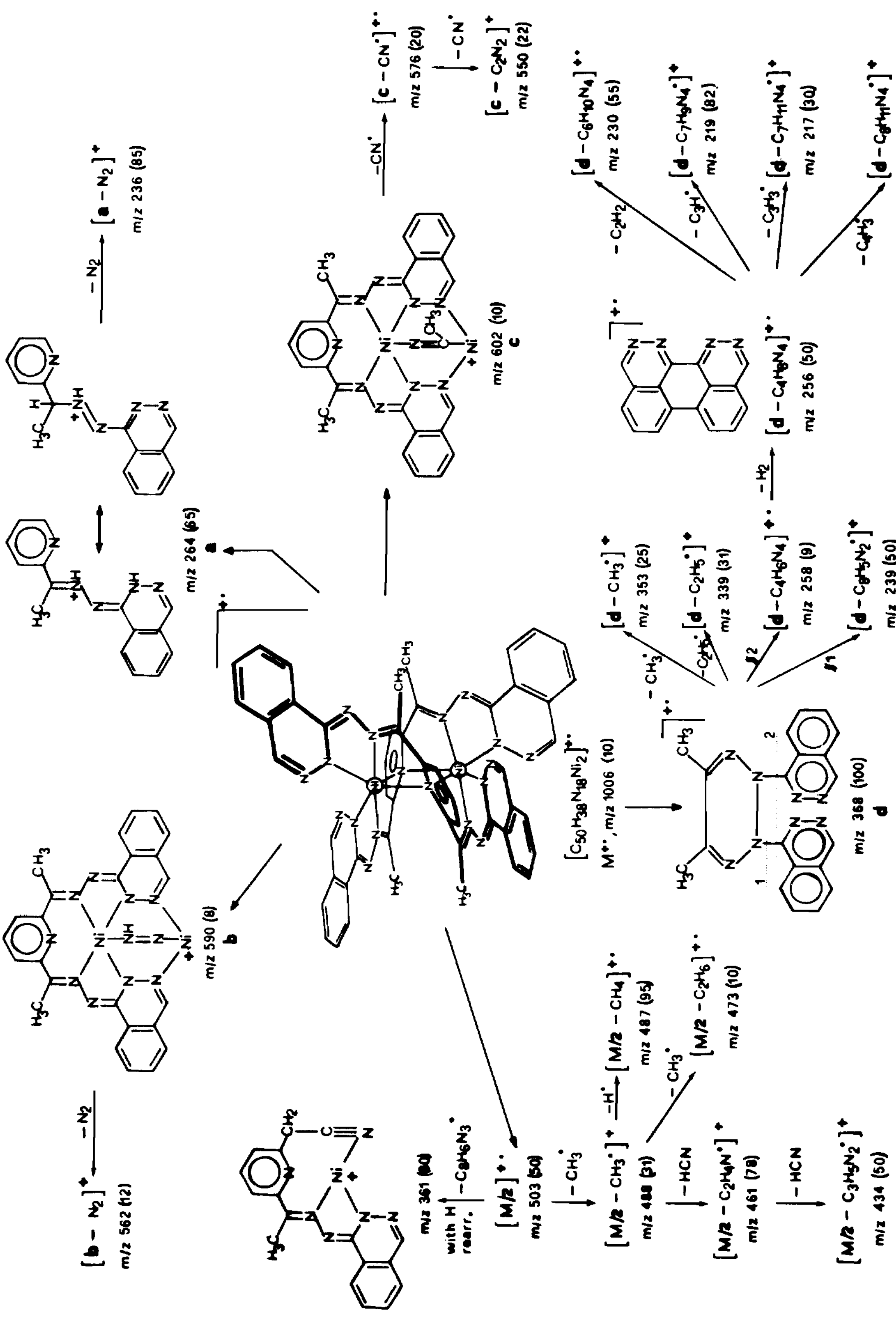


Fig. 2. The 70 eV mass spectra of the complex $[LNi]_2$ (**2**): in the upper part as obtained by direct inlet probe heating at 350 °C, while in the lower part as obtained by laser induced vaporization of the sample.


[C50H38N18Ni2]+•
M+•, m/z 1006 (10)
m/z 264 (65)
a
−N2
[a − N2]+
m/z 236 (85)
m/z 590 (8)
b
−N2
[b − N2]+
m/z 562 (12)
m/z 602 (10)
c
−CN•
[c − CN•]+•
m/z 576 (20)
−CN•
[c − C2N2]+
m/z 550 (22)
m/z 368 (100)
d
−CH3•
[d − CH3•]+
m/z 353 (25)
−C2H5•
[d − C2H5•]+
m/z 339 (31)
f2
[d − C4H6N4]+•
m/z 258 (9)
f1
[d − C9H5N2•]+
m/z 239 (50)
−H2
[d − C4H8N4]+•
m/z 256 (50)
−C2H2
[d − C6H10N4]+•
m/z 230 (55)
−C3H•
[d − C7H9N4•]+
m/z 219 (82)
−C3H3•
[d − C7H11N4•]+
m/z 217 (30)
−C4H3•
[d − C8H11N4•]+
m/z 205 (98)
[M/2]+•
m/z 503 (50)
with H rearr.
−C8H6N3•
m/z 361 (80)
−CH3•
[M/2 − CH3•]+
m/z 488 (31)
−H•
[M/2 − CH4]+•
m/z 487 (95)
−CH3•
[M/2 − C2H6]+•
m/z 473 (10)
−HCN
[M/2 − C2H4N•]+
m/z 461 (78)
−HCN
[M/2 − C3H5N2•]+
m/z 434 (50)

Scheme 3.

stable product ions. The observed decompositions of ionic species at *m/z* 256 account for its fully aromatic character. It is noteworthy that the formation of the ionic species at *m/z* 368 gives direct information about the coordination of the nickel(II) ion. In fact the ligand H_2L contains two potential coordination 'compartments' [6], one of which includes the pyridine, the two hydrazonic and the two phthalazinic (position 2) nitrogen atoms, while the other compartment includes only the two phthalazinic (position 3) nitrogen atoms. Thus the formation of the species at *m/z* 368 can be reasonably explained as a concerted metal assisted cyclization mechanism, only possible with the metal in the first coordination compartment.

(iv) The formation of abundant $M/2^{+\cdot}$ ions, containing just one Ni atom at *m/z* 503. Further fragmentations consist in sequential losses of $CH_3^{\cdot}$ (leading to ionic species at *m/z* 488 and 473) and HCN (leading to ionic species at *m/z* 461 and 434), as expected by the presence of $CH_3{-}C{=}N{-}$ moieties, and in the cleavage of one N—N hydrazonic bond with H-rearrangement, which gives rise to ionic species at *m/z* 361.

All the fragment ions related to mono- and binuclear nickel species have been confirmed by analysis of their isotopic clusters.

Even though, at this stage, we cannot absolutely verify if the fragmentations observed for the samples are due only to EI or to the two combined excitation systems, the low thermal decomposition of the samples (as compared with that observed by using conventional heated direct insertion probe) and the reproducibility of the data have shown the high performances of the laser induced vaporization technique in the characterization of the high-melting coordination compounds. Now we are trying to extend this technique to other classes of coordination compounds, mainly to ionic complexes. This could be the electron technique for the determination of molecular ions, where the low solubilities of the samples prevent any molecular weight measurement in solution.

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