Mass spectrometry of coordination compounds of transition metals with tetradentate ligands. 11. Isomeric quasi-macrocyclic Ni(II) complexes based on S-substituted isothiocarbohydrazides and the structure of "small" ions derived from them[1]

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Abstract

Two series of bonding isomers of Ni(II) coordination compounds with tetradentate quasimacrocyclic ligands based on S-substituted isothiocarbohydrazides were characterized by electron impact (EI) mass spectrometry and by tandem mass spectrometry methods. Conventional EI mass spectra were more *isomer specific* than metastable ion (MI) and collision induced dissociation (CID) mass spectra of the molecular ions. The MI (and CID) mass spectra of the isomers were very similar. This effect resulted from a facile randomization of Ni–N bonds in the ions possessing low internal energies, prior to their dissociation. The compounds were found to be convenient precursors for coordinatively unsaturated metal-containing ions, $[NiL_n]^+$ and $[RNiL_n]^+$ ($n = 1, 2$; $L = NCCH_3$, $NCSCH_3$; $R = OH$, NO). Most of these species had a structure of mono- or disolvated nickel ion. The dissociation of $[HONiNCCH_3]^+$ ions was consistent with the formation of two isomers: one corresponding to the $[HONi]^+$ ion solvated by acetonitrile and the other is a complex of H_2O with $[NiNCCH_2]^+$. A structure of $[HO,Ni,(NCCH_3)_2]^+$ ions was best represented by a five-membered cycle formed by two acetonitrile units and the metal atom with the OH group attached to one of the nitrogen atoms. (Int J Mass Spectrom 193 (1999) 131–141) © 1999 Elsevier Science B.V.

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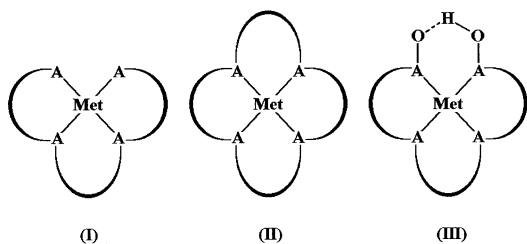
1. Introduction

In our previous papers we reported mass spectral characteristics of a variety of coordination compounds of bivalent metals with tetradentate chelating ligands (open-contour, structure **I**) and tetradentate macrocyclic ligands (closed-contour, structure **II**) [1–12]. Complexes of type **I** have three metallocycles, whereas the compounds of type **II** have four metallocycles surrounding the metal atom. Both **I** and **II** showed abundant molecular and other metal-containing ions, whereas peaks due to ions having no metal

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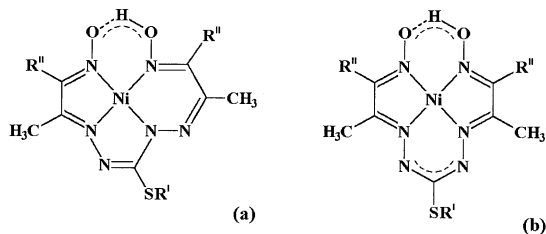[1] For previous communications see [1]–[10] in reference section.

Diagram 1.

(A = donor atom; Met = metal atom)

R^I= CH$_3$, R^{II}= H (1a); R^I= CH$_3$, R^{II}= H (1b);

R^I= CD$_3$, R^{II}= H (2a); R^I= CD$_3$, R^{II}= H (2b);

R^I= CH$_3$, R^{II}= CH$_3$ (3a); R^I= CH$_3$, R^{II}= CH$_3$ (3b);

R^I= CD$_3$, R^{II}= CH$_3$ (4a); R^I= CD$_3$, R^{II}= CH$_3$ (4b);

R^I= C$_2$H$_5$, R^{II}= H (5a); R^I= C$_2$H$_5$, R^{II}= H (5b);

R^I= C$_2$H$_5$, R^{II}= CH$_3$ (6a); R^I= C$_2$H$_5$, R^{II}= CH$_3$ (6b);

R^I= CH$_2$C$_6$H$_5$, R^{II}= CH$_3$ (7a); R^I= CH$_2$C$_6$H$_5$, R^{II}= CH$_3$ (7b).

Diagram 2.

atom were only rarely present in their electron impact (EI) mass spectra. These substances were also characterized by the formation of intense peaks of doubly charged ions. High stability of complexes **I** and **II** to electron impact was assigned to the effective distribution of the internal energy on the multiple vibrational degrees of freedom of the ligand and to the ability of the metal atom to change its oxidation state [1–12].

In the present work, the EI mass spectra of compounds of type **III** will be discussed. Similar to **I** and **II**, complexes of type **III** are highly conjugated systems where the metal atom and the ligand form three metallocycles and one quasimetallocycle; the latter is provided by a hydrogen bridge between two oxygen atoms. One of the goals of this study was to apply mass spectrometry for the identification of isomeric complexes, **1a** and **1b**, **2a**, and **2b**, etc. Complexes of the **a** series contain two six- and two five-membered metallocycles with the alternation (6:6:5:5), whereas compounds of the **b** series possess the (6:5:6:5) metallocycle sequence (one of the six-membered metallocycles for both isomers has a hydrogen bridge). We were also looking for precursors for relatively simple coordinatively unsaturated metal-containing ions, such as solvated nickel ions, [NiL$_n$]$^+$ (*n* = 1, 2; L = NCCH$_3$, NCSCH$_3$) and [RNiL$_n$]$^+$ (R = OH, NO). These species are of special interest with regard to their role as potential intermediates in solution chemistry and in the catalysis. Compounds of type **III** turned out to be convenient precursors for these ions and we studied their structures using tandem mass spectrometry methods.

2. Experimental

Coordination compounds **1–7** were synthesized by the procedure described in [13]. Deuterated derivatives **8a**, **8b**, **9a**, and **9b** were obtained by refluxing solution of **3a**, **3b**, **6a**, or **6b**, respectively, in chloroform with CD$_3$OD for about 3 h. The synthesis of the Pd-containing compound **10** was performed by the procedure similar to **3a** and **3b**. Note that for Pd only one isomer has been obtained. The **10b** structure was assigned from the results of the nuclear magnetic resonance (NMR) study [14] and from the analysis of the EI mass spectrum.

Thermal transformations of **a** and **b** bond isomer

R^I= CH$_3$ (8a); R^I= CH$_3$ (8b);
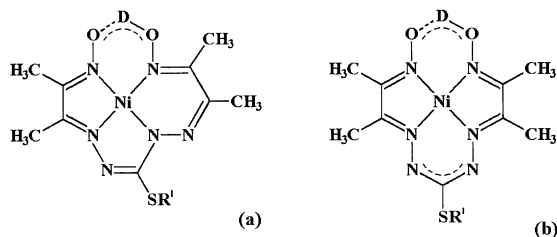
R^I= C$_2$H$_5$ (9a); R^I= C$_2$H$_5$ (9b).

Diagram 3.

pairs were studied by heating them up to the temperature of their decomposition. The latter always exceeded the temperature where these compounds were evaporated into the ion source of the mass spectrometer. Heated samples were analyzed by the thin-layer chromatography method after each 15–20 °C of the increase in temperature. Only one spot was observed on all thin-layer chromatograms, indicating no thermal interconversion of the isomers.

The EI mass spectra were obtained on a double-focusing mass spectrometer MX-1320 (Analitpribor, Sumy) and on a ZAB-SE machine (VG Analytical, Manchester, UK). The compounds were introduced to the ion source of the mass spectrometer using a direct inlet probe. The temperature of the inlet system was 180–220 °C, the temperature of the ionization chamber was 250 °C, emission current 10 μA, ionizing electron energy 70 eV. Monoisotopic mass spectra were calculated from the experimental mass spectra by using AELITA and ISOMETA programs [15].

Tandem mass spectrometry experiments were carried out on a modified triple-sector VG Analytical ZAB-2F mass spectrometer [16] with magnetic sector/electric sector/electric sector (BEE) geometry. The data acquisition was performed using the ZABCAT program (Mommers Tech., Ottawa, Ontario, Canada) [17]. The metastable ion (MI) and collision induced dissociation (CID) mass spectra were recorded by scanning the voltage on the first or the second electrostatic analyzers (ESA). Oxygen was used as target gas in the CID experiments. The pressure of O_2 in the second collision cell of the second field free region (2-FFR) was adjusted to provide 10%–15% reduction (90%–85% T) of the main ion beam. In triple mass spectrometry (MS/MS/MS) experiments, ions generated from metastable or collisionally excited precursors in the 2-FFR were mass selected using the first ESA, transmitted into the 3-FFR and then collisionally activated (He; 85% T).

MI mass spectra of molecular ions of some compounds were also recorded on a reversed geometry mass spectrometer Varian MAT-112. The results were similar to the MI mass spectra obtained on the ZAB-2F machine.

3. Results and discussion

3.1. EI mass spectra

The EI mass spectra of compounds **1–7** are listed in Table 1. Molecular ions ($[M]^{+}$) were very abundant in all cases. Their contribution to the total ion current was higher than 15%. Intense peaks of doubly charged molecular ions were also observed. Similar results have been observed for other highly conjugated complexes, such as complexes of the types **I** and **II** [1–12], porphirines and phtalocyanines [18].

Molecular ions of **1–7** showed two types of dissociation. The first was the fragmentation of thioalkyl group, R′S, resulting in losses of HS·, SCH_2, (R′ − H) or {(R′ − H) + NO}. These processes were similar to the fragmentation of other thioalkyl substituted coordination compounds of types **I** and **II**, and related complexes [1–12]. They required a hydrogen rearrangement and their overall yield was very small.

Simple bond cleavage in peripheral groups, which would result in a loss of R′S·, R″ or CH·$_3$, was not detected in the EI mass spectra of compounds **1–6**. Only the EI mass spectrum of **7** displayed abundant peaks of organic ions, $[C_7H_7]^{+}$, originating from a simple S–C bond cleavage.

A loss of 30 mass units was observed from molecular ions of all compounds studied in this work. This process could correspond to a loss of NO·, C_2H_6 or $2CH_3$. Metastable and collision induced dissociation of mass selected molecular ions of **1a**, **1b**, **3a**, **3b**, **5a**, **5b**, **6a**, and **6b** was examined to identify the origin of $[M − 30]^{+}$ ions. The MI and CID mass spectra displayed peaks of $[M − 30]^{+}$ ions and no signals corresponding to $[M − 15]^{+}$ ions (see, e.g. Figs. 1 and 2). Also the CD_3 derivatives of **2a**, **2b**, **4a**, and **4b** did not contain peaks due to a 36 Da loss in their MI mass spectra. From these observations we conclude that $[M − 30]^{+}$ ions originated from the loss of NO·.

The second type of dissociation reactions was characterized by the fragmentation of quasimacrocyclic ligand skeleton starting with H–O bond cleavage and followed by N–O, N–C, C–C, or N–N bond ruptures. Similar reactions have been observed for molecular ions of mono- and dioximates of bivalent

Table 1
Electron impact mass spectra (70 eV) of compounds **1–7**

Ions	1a		1b	2a		2b	3a		3b	4a		4b	5a		5b	6a		6b	7a		7b
	m/z[a]	I (%)[b]	I (%)	m/z	I (%)	I (%)	m/z	I (%)	I (%)	m/z	I (%)	I (%)	m/z	I (%)	I (%)	m/z	I (%)	I (%)	m/z	I (%)	I (%)
$[M]^{+\bullet}$	314	100.0	100.0	317	100.0	100.0	342	100.0	100.0	345	100.0	100.0	328	100.0	100.0	356	100.0	100.0	418	100.0	100.0
$[M-O]^+$	298	2.2	14.8	301	4.0	18.0	326	2.0	11.0	329	2.7	14.0	312	1.0	14.0	340	3.5	9.2	402	8.1	13.5
$[M-OH]^+$	297	0.2	0.1	300	0.1	0.2	325	0.5	0.8	328	1.5	2.0	311	—	1.0	339	1.0	1.0	—	—	—
$[M-C_2H_4]^+$	—	—	—	—	—	—	—	—	—	—	—	—	300	24.0	20.0	328	11.0	11.0	—	—	—
$[M-NO]^+$	284	14.3	14.3	287	11.0	11.0	312	7.5	8.0	315	8.8	8.6	298	3.0	3.0	326	5.0	3.0	—	—	—
$[M-NOH]^+$	283	0.3	0.5	286	0.1	2.0	311	1.0	6.0	314	0.1	2.0	297	0.3	6.0	325	0.2	2.0	—	—	—
$[M-OH-CH_3]^+$	282	0.1	0.2	285	0.1	—	310	0.7	4.0	313	1.0	2.0	—	—	—	324	0.5	1.5	—	—	—
$[M-SY]^{+\bullet}$[c]	281	0.7	0.7	283	0.3	—	309	0.5	2.0	311	1.0	1.0	295	9.0	8.0	323	7.5	7.5	385	32.4	24.2
$[M-NCCH_3]^+$	—	—	—	—	—	—	301	—	1.0	304	1.8	1.0	—	—	—	315	0.5	—	—	—	—
$[M-SCY_2]^+$	268	0.1	—	269	0.1	—	296	—	—	299	1.0	1.0	282	0.2	(7.0)d	310	1.0	(4.6)	—	—	—
$[M-NO_2]^+$	268	—	6.8	271	—	6.8	296	—	4.2	297	1.0	5.0	282	—	(7.0)d	310	—	(4.6)	—	—	—
$[M-NO-C_2H_4]^+$	—	—	—	—	—	—	—	—	—	—	—	—	270	3.6	4.0	298	1.5	2.2	—	—	—
$[M-NO-NO]^+$	254	0.3	—	—	—	—	—	—	—	—	—	—	—	—	—	296	1.0	1.0	—	—	—
$[M-NO-R''CCCH_3]^+$	244	0.7	0.6	247	0.3	—	244	6.0	6.0	247	6.0	6.0	244	12.0	1.0	—	—	—	—	—	—
$[M-O-NCR''-NCCH_3]^+$	230	8.0	11.0	233	8.0	5.7	—	—	—	—	—	—	258	12.0	12.0	258	11.2	13.5	320	37.8	22.1
$[M-NO-NO-R''CCCH_3]^+$	214	0.1	1.0	217	0.3	0.6	—	—	—	—	—	—	228	—	2.0	—	—	—	—	—	—
$[R'SC(N)NNCCH_3Ni]^+$	186	3.8	6.0	189	3.8	4.3	186	4.0	8.0	189	6.0	6.0	—	—	—	200	7.0	4.0	—	—	—
$[CY_2SC(N)NNCCH_3Ni]^+$	185	1.0	1.0	187	1.0	1.0	185	1.0	1.0	187	2.0	2.0	—	—	—	—	—	—	—	—	—
$[R'SCNNiNCCH_3]^+$	172	7.0	11.0	175	8.0	7.0	172	7.0	7.0	175	6.5	10.0	186	9.0	10.0	186	6.5	7.0	—	—	—
$[ONNiNCSR']^+$	161	6.0	8.0	164	6.5	5.3	161	13.0	6.0	164	14.0	18.0	175	3.0	3.0	175	8.0	10.0	—	—	—
$[HCNNiNCSR']^+$	158	4.5	8.0	161	3.0	3.3	—	—	—	—	—	—	172	2.0	3.0	—	—	—	—	—	—
$[HONi(NCR')NCCH_3]^+$	143	26.0	44.5	143	43.0	28.0	157	10.8	8.0	157	9.0	13.0	143	40.0	42.0	157	17.0	35.0	—	—	—
$[NiNCSR']^+$	131	25.0	35.0	134	45.0	26.0	131	20.0	10.0	134	23.0	23.0	145	16.0	16.0	145	14.0	18.0	—	—	—
$[ONNiNCCH_3]^+$	129	10.0	10.0	129	9.0	20.0	129	16.0	16.0	129	16.0	18.0	129	—	23.0	129	22.0	57.0	—	—	—
$[Ni(NCR'')NCCH_3]^+$	126	8.0	18.0	126	6.0	13.0	140	13.0	12.0	140	13.5	20.0	126	13.0	6.0	140	24.0	59.3	—	—	—
$[HONiNCCH_3]^+$	116	10.0	18.0	116	14.5	16.0	116	13.0	17.0	116	15.0	20.0	116	23.0	23.0	116	18.0	42.0	—	—	—
$[ONNiNCH]^+$	115	5.0	6.0	115	6.0	6.0	—	—	—	—	—	—	115	6.0	10.0	—	—	—	—	—	—
$[HONiNCH]^+$	102	4.0	5.0	102	5.0	7.0	—	—	—	—	—	—	102	11.0	15.0	—	—	—	—	—	—
$[NiNCCH_3]^+$	99	53.0	128.0	99	83.0	97.0	99	72.0	171.0	99	61.0	109.0	99	115.0	160.0	99	82.5	220.0	99	216.0	57.1
$[NiNCCH_2]^+$	98	8.0	12.0	98	15.0	13.0	98	5.0	5.0	98	3.0	10.0	98	13.0	15.0	98	4.0	4.0	—	—	—
$[NiNO]^+$	88	7.0	12.0	88	12.0	18.0	88	4.0	6.0	88	3.0	4.0	88	10.0	15.0	88	3.0	3.5	—	—	—
$[NiNCH]^+$	85	18.0	37.0	85	28.0	33.0	—	—	—	—	—	—	85	30.0	45.0	—	—	—	—	—	—
$[NiOH]^+$	75	9.8	18.0	75	18.0	2.0	75	9.0	10.0	75	9.0	10.0	75	16.0	16.0	75	9.0	21.0	—	—	—
$[Ni]^+$	58	36.0	72.0	58	60.0	60.0	58	28.0	45.0	58	25.0	38.0	58	42.0	62.0	58	27.1	60.0	—	—	—
$[M]^{2+}$	157	2.0	—	158.5	1.6	2.0	171	5.0	3.0	172.5	3.1	5.7	164	1.4	3.0	178	2.5	2.8	—	—	—
$[C_7H_7]^+$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	91	297.0	168.0

[a] m/z values are given for ions containing ^{58}Ni, ^{12}C, ^{16}O, ^{14}N, and ^{1}H isotopes.

[b] Peaks with relative intensities less than 0.1% are not listed.

[c] Y = H for **1a**, **1b**, **3a**, **3b**, **5a**, **5b**, **6a**, **6b**, **7a**; Y = D for **2a**, **2b**, **4a**, **4b**.
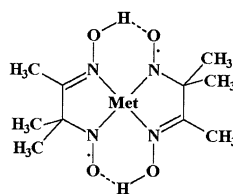
[d] Summed intensity for $[M-SCH_2]^+$ and $[M-NO_2]^+$ ions.
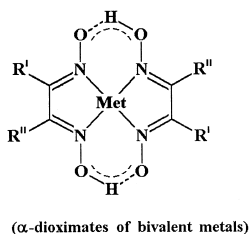
(α-dioximates of bivalent metals)

(IV)

Diagram 4.

(Met(II) complexes of
1,2-hydroxyaminooxime derivatives)

(V)

Diagram 5.

metals (**IV**; see, e.g. [18–20] and references cited therein). The behavior of oximate fragment, O–H . . . O, in molecular ions of **1–7** was similar to, but not the same as that of dioximates of type **IV**. Among the dissociations common for the ionized **1–7** and dioximates were losses of OH˙, NOH and the formation of $[HONiL_n]^+$ ions (Table 1). In these reactions, the hydrogen atom of the hydroxyl group endured its position at the oxygen atom. It was clearly indicated by the mass spectra of compounds **8a**, **8b**, **9a**, and **9b**, in which the hydrogen atom was replaced by deuterium. The ions, having HO group in the EI mass spectra of **3a**, **3b**, **6a**, and **6b**, were shifted by 1 Da to heavier masses in the mass spectra of the corresponding DO analogs, whereas ions having no HO group retained their position on the mass scale.

Unlike the above mentioned reactions where the hydrogen atom retains its position to one of the oxygen atoms, the formation of $[M - NO_2]^+$ ions is preceded by a hydrogen rearrangement. It should be noted that peaks due to $[M - NO_2]^+$ ions were found in the EI mass spectra of the **b** series of **1–7** compounds, whereas the mass spectra of the **a** isomers did not display such peaks (Table 1). Tandem mass spectrometry experiments with mass selected $[M]^+$, $[M - O]^+$ and $[M - NO]^+$ ions demonstrated that all of them were precursors for $[M - NO_2]^+$ ions. Thus, the latter originated from the direct loss of NO_2, from the consecutive losses of NO and O, and by a loss of an oxygen atom followed by expulsion of NO. The loss of NO_2 as an intact unit must have involved a shift of oxygen atom from one of the nitrogen atoms to another.

The most intense peaks in the EI mass spectra of

compounds **1–7** corresponded to $[M]^{˙+}$, $[NiNCCH_3]^+$ and $[NiNCR'']^+$. $[Ni]^+$ and $[NiNCSR']^+$ ions were also abundant in the EI mass spectra of **1–6**. All these ions were a result of multi-stage dissociations, involving a rupture of various metal–ligand bonds and bonds within the ligand. The high intensity of these fragments is indicative of their high stability.

One of the interesting features of the mass spectral behavior of complexes **1–6** was that some fragment ions displaying a very low abundance in the EI mass spectra were rather intense in the MI mass spectra. For example $[M - NO]^{˙+}$ ions and the ions formed from them by losses of NO, $R''CCCH_3$, and $CH_3CCR''NO$ (or $\{CH_3CCR'' + NO\}$) were important products of the metastable dissociation of molecular ions of **1–6**, but they displayed a very low abundance in the EI mass spectra. This effect can be rationalized in terms of the energy content of the ions produced from molecular ions in the ion source and in the field-free region. The dissociation of the molecular ions in the ion source most likely resulted in $[M - NO]^{˙+}$ ions whose internal energy exceeded the (low) barrier for their (further) dissociation. $[M - NO]^{˙+}$ ions originating from the metastable molecular ions possessed lower internal energy than their counterparts from ion source generated analog. As a result they had better chances to survive further dissociation. Note that similar behavior has been observed for the Ni-containing analogue of the **V** [21]. The EI mass spectrum of this complex did not show $[M - 2NO]^+$ ions, whereas the loss of NO from metastable $[M - NO]^{˙+}$ ions gave rise to a stable $[M - 2NO]^+$ species.

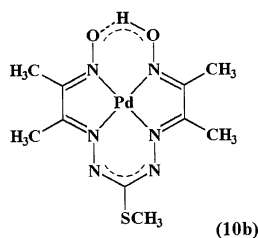Unlike the Ni-containing complex **V**, the EI mass

Diagram 6.

spectrum of its palladium-containing analog showed intense peaks for $[M - 2NO]^+$ ions [21]. The difference in mass spectral behavior of the two complexes likely arose from a higher stability of Pd–C relative to Ni–C bonds. Formation of σ-metal–carbon bonds is expected after the loss of two NO molecules from the molecular ions. As a result, the dissociation of the ionized Pd-containing analog of compound **V** produced abundant $[M - 2NO]^+$ ions.

The EI mass spectrum of another Pd-containing complex, **10b** did not show peaks for $[M - 2NO]^+$ ions. The major differences between the dissociation of the Ni-containing complex **3b** and its Pd-containing analog **10b** appeared in those mass regions where the latter displayed intense peaks for $[Met(NCCH_3)_2NO]^+$ and $[Met(CCH_3)_2NO]^+$ ions (compare Tables 1 and 2). These results again illustrate the effect of the metal atom on the mass spectral fragmentation of coordination complexes. The nature of the organic ligand is an another significant factor, determining what ions can be formed.

In summary, the mass spectral behavior of complexes **1–10** is similar to that of other coordination compounds having highly conjugated polyheterocyclic ligands [1–12,18]. The positive charge in their molecular ions is efficiently delocalized between the central metal atom and the ligand. As a result, the molecular ions of these compounds are very stable and doubly charged ions can be easily produced. Surprisingly, the most abundant fragmentations of the molecular ions involved a splitting the quasi-macrocyclic ligand apart rather than the dissociation of "peripheral" groups (substituents).

Table 2
Electron impact mass spectrum (70 eV) of compound **10b**

Ions	m/z^a	Rel. int. (%)
$[M]^{.+}$	390	100.0
$[M - O]^+$	374	27.8
$[M - NO]^+$	360	17.2
$[M - NOH]^+$	359	0.6
$[M - OH - CH_3]^+$	358	0.6
$[M - SH]^+$	357	0.7
$[M - SCH_2]^+$	344	$(6.7)^b$
$[M - NO_2]^+$	344	$(6.7)^b$
$[M - O - NCCH_3 - NCCH_3]^+$	292	3.4
$[H_3CSC(N)NNCCH_3Pd]^+$	234	2.5
$[H_2CSC(N)NNCCH_3Pd]^+$	233	5.0
$[ONPd(NCCH_3)_2]^+$	218	13.0
$[ONPdNCSCH_3]^+$	209	2.5
$[HOPd(NCCH_3)_2]^+$	205	21.7
$[Pd(CCH_3)_2NO]^+$	190	20.0
$[Pd(NCCH_3)_2]^+$	188	5.0
$[PdNCSCH_3]^+$	179	1.7
$[ONPdNCCH_3]^+$	177	31.7
$[HOPdNCCH_3]^+$	164	5.0
$[PdNCCH_3]^+$	147	75.0
$[PdNO]^+$	136	29.2
$[PdOH]^+$	123	8.0
$[Pd]^+$	106	50.0
$[M]^{2+}$	195	2.5
Other Pd-containing ions:	291	2.0

^{a} m/z values are given for ions having the most abundant isotopes (^{106}Pd, ^{12}C, etc.).
^{b} Summed intensity for $[M - SCH_2]^+$ and $[M - NO_2]^+$ ions.

3.2. Recognition of the isomers

The MI mass spectra of the isomers of the types **a** and **b** were very similar. The observed differences in relative abundances of fragment ions did not allow assignment of the mass spectrum to the structure of the isomer (see, e.g. Fig. 1 for **3a** and **3b**). The molecular ions of the isomers also displayed comparable CID mass spectra (Fig. 2).

Distinctive differences between **a** and **b** type isomers were observed in the EI mass spectra. For example, a loss of NO_2 (and/or {NO + O}, {O + NO}) from $[M]^{.+}$ was detected only for the **b** type isomers (Table 1). The EI mass spectra of these isomers also displayed more abundant $[M - O]^+$ ions than those of the corresponding **a** type complexes. The intensities of peaks for $[NiNO]^+$, $[NiNCCH_3]^+$, and $[HONiNCCH_3]^+$ ions were also

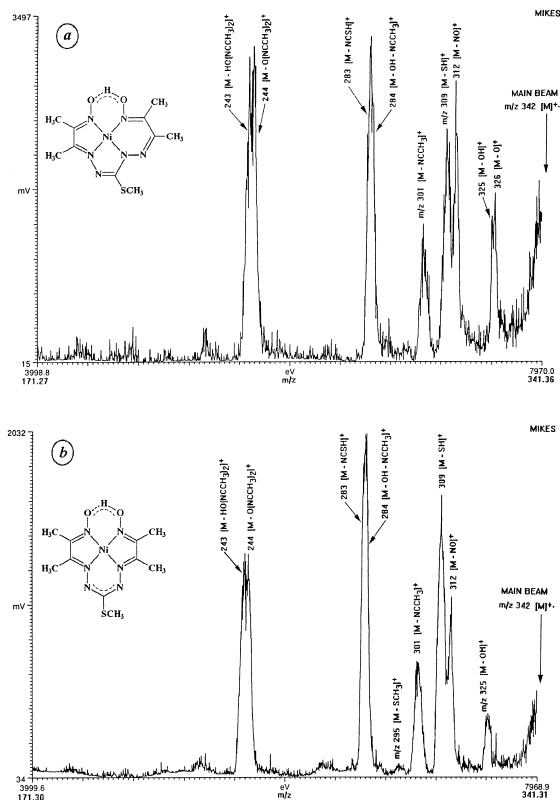Fig. 1. Metastable ion mass spectra of **3a** (*a*) and **3b** (*b*).

Fig. 2. Collision induced dissociation (O$_2$, 90% T) mass spectra of **3a** (*a*) and **3b** (*b*).

different. They were more abundant in the mass spectra of the **b** isomers (Table 1), which was consistent with their formation from [M − O]$^+$ and [M − NO$_2$]$^+$ ions.

The similarity in the MI and CID mass spectra of the isomers, and the difference in their EI mass spectra can be rationalized by the internal energies of ions examined in various mass spectral experiments. The (molecular) ions from the field-free region represented "long-lived" species whose internal energy is lower or just above the dissociation limit(s). This energy however, was sufficient for the interconversion between isomers by the "randomization" of Ni–N bonds resulting in a loss of the isomer identity. The energy for such isomerization should be lower than the activation energies of isomer specific dissociations. The latter takes place in energy rich ions, e.g. in the species decomposing in the ion source of the mass spectrometer.
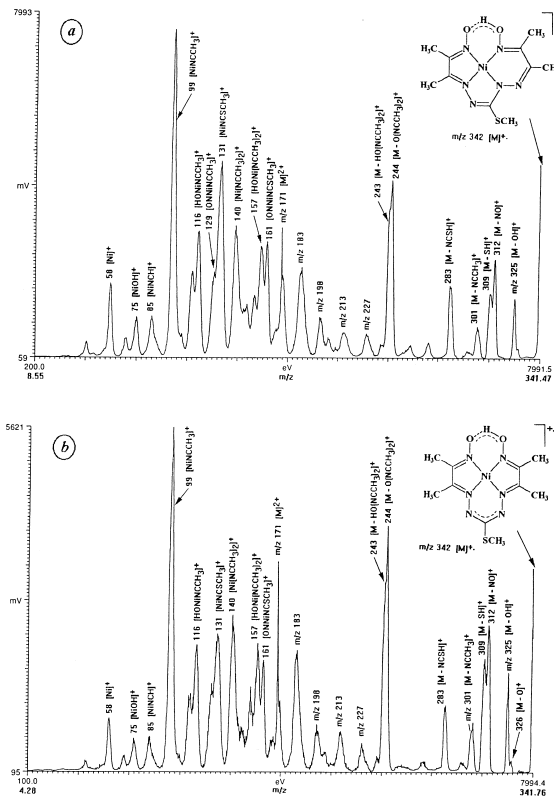
The presence of [M − NO$_2$]$^+$ ions in the mass spectrum of the Pd-containing complex **10** was indicative for the structure of the **b** type by the analogy to its Ni-containing analog. The EI mass spectrum was a useful addition to the NMR data [14] of the complex **10** in the assignment of its structure.

In summary, the compounds of **a** series can be best distinguished from their **b** isomers using conventional EI mass spectra. The MI and CID mass spectra of molecular ions were less informative as a tool for the identification of these compounds, but they were important for the identification of ion origin and dissociation sequences.

3.3. Structures of "solvated" Ni$^+$ ions

The EI mass spectra of **1–7** and the CID mass spectra of their molecular ions showed a number of

low mass nickel-containing fragments. Their structures might be represented as RNi^+ or Ni^+ ions solvated with neutral molecules. Ions of this type, e.g. metal ions solvated by nitriles have been generated by electron impact induced dissociation of a variety of coordination compounds: α-dioximates of metals (see, e.g. [18–20]), Ni(II) and Pd(II) complexes of 1,2-hydroxyaminooxime derivatives [21], complexes of various metals with thiosemicarbazones of aliphatic ketones [1–4,6,7,9,11], and 14-membered hexaazamacrocyclic [8,11,12], as well as 14- and 15-membered octaazamacrocyclic derivatives of Ni(II) [5,11]. Other methods of generating metal ions solvated by nitrile molecule(s), including ion–molecule reactions are described in [22–29], and references cited therein.

We tested structures of some "simple" Ni-containing ions originating from the ionized **1–7** by using tandem mass spectrometry (MI and CID) experiments. The ions under investigation contained NO, OH, HCN, CH_3CN, and CH_3SCN groups connected directly to the metal atom or forming ligands of a higher complexity. To provide the best interpretation of the experimental results it is essential to consider bond strength between the above molecules and the Ni^+ ion.

Experimental measurements of bond dissociation energies (BDEs) have been performed for the Ni^+–NO bond. The $D(Ni^+$–NO) value was determined as 54 kcal mol^{-1} [30]. The Ni^+–NO bond cleavage in two-ligand systems, LNi^+NO, required lower energy, $\sim$42 (L = C_5H_5 [31,32]) and 29 (L = NO [31]) kcal mol^{-1}. The dissociation energy for the Ni^+–OH bond has been estimated to be $\sim$56 kcal mol^{-1} [33].

Several authors [28,34–36] have measured the affinities of Ni-containing ions to nitriles, including the determination of relative double metal–ligand BDEs [34,36]. In all cases higher alkyl derivatives showed a stronger binding to the Ni^+ ion than molecules with fewer carbon atoms. For example, HCN was always weaker bound than CH_3CN to metal ions. No experiments have been performed to compare directly BDEs for nitriles and OH. The results for $C_5H_5Ni^+L$ ions showed, however, that both HCN and
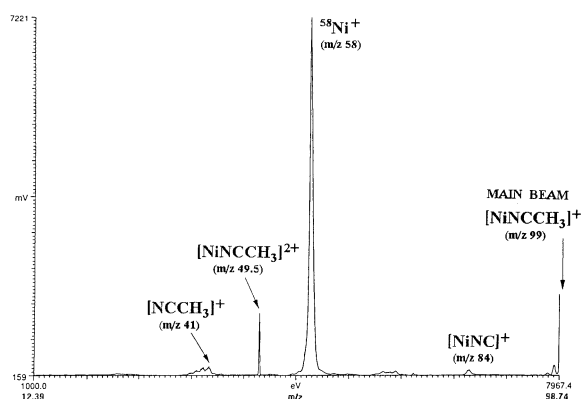

Fig. 3. Collision induced dissociation (O$_2$, 90% T) mass spectrum of [NiNCCH$_3$]$^+$ ions.

CH_3CN were bound stronger to the metal atom than NO [35].

No data on Ni^+–NCSCH$_3$ bond dissociation energies were available. Nevertheless, we believe that NCSCH$_3$ should be stronger bound to the transition metal ion than acetonitrile. The presence of the sulfur atom should increase electron-donating properties of SCH$_3$ relative to the CH$_3$ group [37]. Also a direct interaction between Ni and S atoms will likely increase the stability of the Ni^+–NCSCH$_3$ bond.

From the above considerations the following trend in Ni^+–L BDEs can be drawn: L = NO < HCN < CH_3CN < CH_3SCN < OH. Certainly, to exclude any doubts concerning this Ni^+–L bond energy order, experimental measurements of BDEs performed in similar conditions would be required. It should also be noted that absolute and relative bond strengths could vary depending on other ligand(s) connected to the metal atom. This general tendency can be nonetheless used effectively for the following assignment of Ni^+-containing ion structures.

The EI mass spectra of all compounds studied in this work displayed intense peaks of $Ni^+(NCCH_3)$ ions. The MI mass spectrum of $Ni^+(NCCH_3)$ was very simple, showing only a peak for the $[Ni]^+$ ion. Collisional activation of $Ni^+(NCCH_3)$ resulted in three additional products (Fig. 3). The observation of a low abundant methyl radical loss was consistent with the previous results by Chen and Miller [25], who assigned this reaction to the metal atom insertion
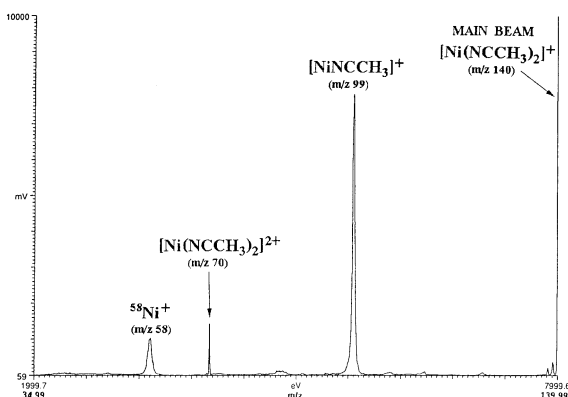
Fig. 4. Collision induced dissociation (O$_2$, 90% T) mass spectrum of [Ni(NCCH$_3$)$_2$]$^+$ ions.

Scheme 1.

into the C–C bond. The other peaks in the CID mass spectrum corresponded to [NiNCCH$_3$]$^{2+}$ and [CH$_3$CN]$^{\cdot+}$ ions; the latter most likely originated from the doubly charged species. Note that Ni$^+$(NCCH$_3$) ions produced by unimolecular dissociation of compounds **1–7** were indistinguishable from their analogues formed by ion–molecule reactions in CH$_3$CN–nickelocene and CH$_3$CN–(acac)$_2$Ni mixtures. These results indicated that in both cases solvated metal ions were formed. The present experiments however, could not distinguish a type of binding of acetonitrile to the metal ion.

The MI mass spectrum of Ni$^+$(NCCH$_3$)$_2$ displayed only one peak corresponding to a loss of one acetonitrile molecule. The collisional activation gave rise to Ni$^+$ ions. Doubly charged ions, [Ni(NCCH$_3$)$_2$]$^{2+}$, were also abundant species in the CID (target gas − O$_2$) mass spectrum (Fig. 4). The CID mass spectrum also showed minor fragments (<1%) corresponding to H$_2$C and HCN losses from CH$_3$CN ligands. The dissociation of Ni$^+$(NCCH$_3$)$_2$ ions was consistent with the structure of disolvated nickel cation, which has been previously generated and characterized by the Fourier transform ion cyclotron resonance (FT-ICR) MS method [36]. A cyclic isomer, **VI**, might have been formed upon the fragmentation of complexes **3a** and **3b** under EI (Scheme 1), but it most likely rearranged to the structure having two separate acetonitrile units prior to the dissociation. The experimental observations were in a good agreement with
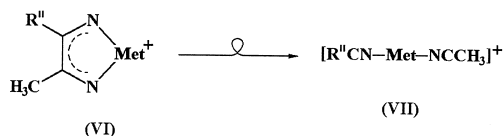
our calculations by the Modified Neglect of Diatomic Differential Overlap (MNDO) method for the [Zn(NCR)$_2$]$^+$ system [38]. The latter predicted that the linear isomer (**VII**) should be the most stable among [Met(NCR)$_2$]$^+$ species.

The MI mass spectra of HONi$^+$NCCH$_3$ ions originating from compounds **1a**, **1b**, **3a**, and **3b** were indistinguishable. The most abundant process (~80%) corresponded to the loss of H$_2$O. The MI mass spectrum of DONi$^+$NCCH$_3$ ions displayed a peak for a loss of HDO, whereas no H$_2$O loss was observed. This result indicated that the H-atom shift from the methyl to the hydroxyl group was irreversible. The other metastable dissociation of HONi$^+$NCCH$_3$ involved a loss of CH$_3$CN. The absence of HO$^\cdot$ loss from the metastable ions was consistent with a stronger Ni$^+$–OH relative to Ni$^+$–NCCH$_3$ bond. Collisional activation of HONi$^+$NCCH$_3$ significantly increased the yield of HONi$^+$ ions. It also produced Ni$^+$NCCH$_3$ ions, but the signal of the latter was very weak. Thus, the dissociation of HONi$^+$NCCH$_3$ ions was consistent with the formation of two structures: one corresponding to the HONi$^+$ cation solvated by acetonitrile molecule and the other is the complex of H$_2$O with Ni$^+$NCCH$_2$ ions. A third structure for these ions, i.e. that having a HONCCH$_3$ moiety as a single ligand, could also be considered. However, the close similarity in the dissociation of ions originating from the precursors with (**3a** and **3b**)
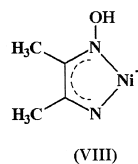

(VIII)

Diagram 7.

and without an HO group attached to acetonitrile fragment (**1a** and **1b**) made that structure as very unlikely.

The dissociation of $HONi^+(NCCH_3)_2$ ions was significantly different from that of the ions having only one acetonitrile group. The most abundant metastable process was a loss of HO. Two other reactions resulted in $HONi^+NCCH_3$ and Ni^+NCCH_3 ions. These observations were in disagreement with the thermochemistry of the Ni^+–ligand bond dissociation because the Ni^+–OH bond is expected to be stronger than Ni^+–acetonitrile bond. For the latter reason a preferable loss of OH over $NCCH_3$ would be very unlikely from the ions having the structure of disolvated $HONi^+$ ions. The experimental observations can be easily rationalized by the cyclic structure **VIII**. This structural unit was present in molecules of all complexes and the corresponding ions could be formed by a loss of the rest of the quasi-macrocyclic ligand. The OH group in the **VIII** ion is not connected to the metal atom and can be easily lost as a radical or together with the $NCCH_3$ unit.

The behavior of the $Ni^+(NCCH_3)(NCSCH_3)$ ion was consistent with the structure of a disolvated nickel cation. The MI mass spectrum of this species displayed two peaks, corresponding to losses of $NCCH_3$ and $NCSCH_3$ in agreement with the structure of disolvated nickel ions. The latter process was ~4 times less abundant, indicating a predicted stronger binding of Ni^+ to $NCSCH_3$ than to $NCCH_3$. The CID mass spectrum displayed a peak for Ni^+ ions. Minor fragments (<1%) were also observed at m/z 145 and m/z 113. They corresponded to the losses of NCH and NCSH from $NCCH_3$ and $NCSCH_3$ groups, respectively.

The MI mass spectra of $ONNi^+NCCH_3$ and $ONNi^+NCSCH_3$ ions were very simple showing only peaks corresponding to a loss of NO. These results indicated that Ni^+–nitrile bonds are stronger than the Ni^+–NO bond in agreement with the general trend in Ni^+–ligand bond dissociation energies.

The results from this part of our study exhibited that the coordination compounds **1–7** are convenient precursors for coordinatively unsaturated metal-containing ions. In most cases structures of these ions are best represented as nickel-containing ions solvated with nitrile(s), $[NiL_n]^+$ ($n = 1, 2$; L = $NCCH_3$, $NCSCH_3$) or $[RNiL_n]^+$ (R = OH, NO). The observation of dissociations opposing the expected trend in metal–ligand bond dissociation energies was indicative of the presence of different types of structures. For example, the metallocyclic structure **VIII** rationalizes well the behavior of "$HONi^+(NCCH_3)_2$" ions.

4. Conclusion

Electron impact ionization of two series of bonding isomers of Ni(II) coordination compounds with tetradentate quasimacrocyclic ligands **1–9** generated very intense molecular ions. Their fragmentation was similar to that of other coordination compounds having highly conjugated macroheterocyclic ligands. The molecular ions underwent two common types of dissociation. The first involved the fragmentation of thioalkyl, R′S, group and their yield was very small. The second type of dissociation resulted in the extensive fission of metal–ligand bonds and bonds (N–O, N–C, C–C, and N–N) of the ligand. These reactions started from the H–O bond cleavage of the quasimetallocycle.

Isomers of **a** and **b** structures can be distinguished by their EI mass spectra. In particular, the presence of $[M - NO_2]^+$ ions was a characteristic for the isomers of the **b** type. The MI (and CID) mass spectra of the isomers were very similar. This effect resulted from a facile randomization of Ni–N bonds in the ions possessing low internal energies, prior to their dissociation.

Complexes of the **III** type proved to be convenient precursors for a variety of relatively simple nickel-containing ions. Structures of these ions were assigned based on their metastable and collision induced dissociations. Most of these species possessed a structure of solvated Ni^+ or RNi^+ ions. The metallocyclic structure **VIII** was suggested for "$HONi^+(NCCH_3)_2$" ions to rationalize the preferable loss of OH over the loss of $NCCH_3$.

Acknowledgements

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