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Notes

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Mass Spectrometric Behavior of Bis(cyanoimino-β-carbonylenolato)nickel(II) Complexes

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In the course of our studies on the activation of cyanogen by metal complexes,[1-5] we discovered the reaction depicted in Scheme I, i.e. a metal-controlled process leading to the formation of a C–C bond under quite mild conditions.

The remarkable consequence of this finding was the achievement of the organic synthetic process converting various β-dicarbonyls into pyrimidines, pyrrolidines, furans, and lactones.[5-7]

We recently described[8] the reaction of [M(β-carbonylenolato)$_2$] complexes (M = Ni, Cu) with C_2N_2 according to Scheme I, but the identification of the ligand configuration of the reaction products proved to be impossible by conventional methods; see Scheme II.

We report here the possibilities offered by mass spectrometry, particularly by the mass-analyzed ion kinetic energy (MIKE) technique, for solving this ligand configurational problem.

The formulas, e.g. [Ni(baC_2N_2)$_2$], indicate the addition–insertion product[9] according to Scheme II.

Results and Discussion

In Table I the main features of the EI mass spectra of the investigated compounds are summarized. In the same table the ion composition assignments, as obtained by exact mass measurements, isotopic compositions, and linked scans, are also reported.

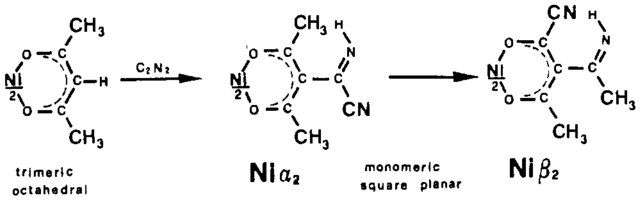
Molecular ions are always present, but their relative abundances are variable, i.e. from 0.02% in the case of [Ni(dpmC_2N_2)$_2$] to 100% for [Ni(eaaC_2N_2)$_2$].

The fragmentation pattern appears to be clearly dependent on the substituent groups, giving good analytical information on the structural identity of the examined compounds. For example, [Ni(dpmC_2N_2)$_2$] shows a fragmentation pattern completely different from those of the other complexes, being mainly governed by decomposition pathways related to the presence of t-C_4H_9 groups; the loss of $C_2H_5O\cdot$ is observed for [Ni(eaaC_2N_2)$_2$] only, and so on.

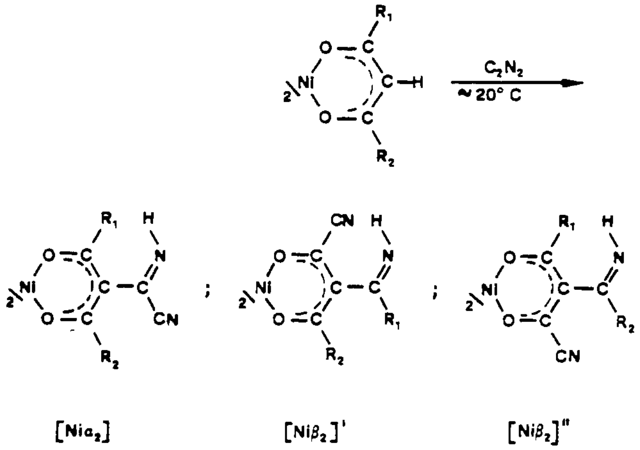
Moreover, an interesting retrosynthetic process,[10] consisting of a primary loss os cyanogen, can be observed for all compounds but [Ni(eaaC_2N_2)$_2$].

In spite of this useful analytical information about the addition compounds, it is impossible to obtain from these spectra unambiguous proof of the [Mβ$_2$]′ or [Mβ$_2$]″ ligand configurations of the investigated species. For instance, the α and β isomers of [Ni(acacC_2N_2)$_2$] give rise to practically identical EI mass spectra at 200 °C, with minor differences in relative abundances only.

Scheme I



Scheme II



For these reasons, MIKE and CAD (collisionally activated decomposition) experiments become essential in order to test the possibilities offered by these mass spectrometric techniques in structure elucidation of this class of compounds.

The MIKE spectra of molecular ions $M^{+\cdot}$ of the title compounds are reported in Table II.

Significant species and processes for the [Mα$_2$], [Mβ$_2$]′, or [Mβ$_2$]″ structures are (i) primary loss of RCNH· radicals, which is strongly indicative of a β structural configuration, and (ii) primary loss of $C_2N_2H\cdot$ radical, which can arise from an α structure only.

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(1) Corain, B.; Del Pra, A.; Filira, F.; Zanotti, G. *Inorg. Chem.* **1979**, *18*, 3523.

(2) Corain, B.; Crotti, C.; Del Pra, A.; Filira, F.; Zanotti, G. *Inorg. Chem.* **1981**, *20*, 2044.

(3) Corain, B.; Basato, M.; Del Zotto, A.; Zanotti, G. *Inorg. Chem.* **1983**, *22*, 2744.

(4) Corain, B.; Basato, M.; Visentin, G.; Zanotti, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1217.

(5) Corain, B.; Basato, M.; Marcomini, A.; Klein, H.-F. *Inorg. Chim. Acta* **1983**, *74*, 1.

(6) Corain, B.; Basato, M.; Klein, H.-F. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 982.

(7) Basato, M.; Corain, B.; Veronese, C. A.; D'Angeli, F.; Valle, G.; Zanotti, G. *J. Org. Chem.*, in press.

(8) Corain, B.; Basato, M.; Ballotta, C.; Ahmed M. *Inorg. Chim. Acta* **1984**, *87*, 105.

(9) In this paper we will use the following abbreviations: acac = acetylacetonate; eaa = ethyl acetoacetate; ba = benzoylacetonate; dbm = dibenzoylmethanate; dpm = dipivaloylmethanate.

(10) Kametani, R.; Fukumoto, F. *Acc. Chem. Res.* **1976**, *9*, 319.

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Table I. EI Mass Spectra[a] of [Ni(β-carbonylenolato-C_2N_2)$_2$] Complexes[b]

ionic species	1	2	3	4	5	6
$[M]^{+\cdot}$	360 (8)	360 (7)	484 (47)	608 (0.1)	420 (100)	528 (0.02)
$[M - CH_3]^+$	345 (2)	345 (2)	469 (2)		405 (18)	
$[M - HCN]^{+\cdot}$	333 (7)	333 (7)	457 (16)	581 (0.05)	393 (7)	
$[M - CH_3CNH]^+$	318 (8)	318 (8)	442 (2)			
$[M - C_2H_5O]^+$					375 (22)	
$[M - C_2N_2]^{+\cdot}$	308 (6)	308 (6)	432 (3)	556 (0.05)		476 (2)
$[M - C_2N_2 - CH_3]^+$	293 (5)	293 (4)				
$[M - C_2N_2 - C_4H_9]^+$						419 (45)
$[M - C_2N_2 - C_4H_9 - HCN]^+$						392 (29)
$[M - (C_2N_2)_2 - C_4H_9]^+$						367 (50)
$[M - (C_2N_2 + C_4H_9)_2]^{+\cdot}$						310 (10)
$[LNi + H]^+$	210 (21)	210 (21)	272 (25)	334 (0.5)	240 (99)	
$[LNi - H]^+$	208 (34)	208 (40)	270 (25)	332 (1)	238 (27)	
$[LNi - CN]^+$	183 (28)	183 (26)	245 (30)	307 (1)	213 (10)	
$[LH]^{+\cdot}$	152 (15)	152 (15)	214 (28)	276 (10)		
$[L]^+$			213 (75)	275 (24)		
$[L - CN]^{+\cdot}$	125 (100)	125 (100)	187 (10)	249 (21)	155 (25)	
$[L - HCN]^+$			186 (100)	248 (100)		
$[LH - CH_2CO]^{+\cdot}$	110 (36)	110 (34)	172 (12)	234 (5)	140 (23)	
$[LH - CH_2COCH_3]^{+\cdot}$	95 (30)	95 (29)	157 (2)	219 (7)	125 (1)	
$[CH_3CO]^+$	43 (80)	43 (80)	43 (70)	43 (5)	43 (90)	
$[C_6H_5CO]^+$			105 (90)	105 (97)		
$[C_4H_9CO]^+$						85 (15)
$[C_4H_9]^+$						57 (99)

[a] m/z (relative intensity). [b] **1** = [Ni(acacC_2N_2)$_2$]α; **2** = [Ni(acacC_2N_2)$_2$]β; **3** = [Ni(baC_2N_2)$_2$]; **4** = [Ni(dbmC_2N_2)$_2$]; **5** = [Ni(eaaC_2N_2)$_2$]; **6** = [Ni(dpmC_2N_2)$_2$].

Table II. MIKE Spectra[a] of Molecular Ions of Compounds **1**-**6**[b]

	compd (ligand confign)					
ionic species	**1** (β)	**2** (β)	**3** (α and β)	**4** (α)	**5** (β)	**6** (α)
$[M - CH_3]^+$	345 (50)	345 (48)	469 (22)		405 (84)	
$[M - HCN]^{+\cdot}$	333 (56)	333 (54)	457 (100)	581 (100)	393 (35)	
$[M - CH_3 - C{=}NH]^{+\cdot}$	318 (13)	318 (12)	442 (15)		378 (25)	
$[M - C_2N_2H]^+$	307 (1)	307 (1)	431 (25)	555 (3)		475 (10)
	238 (8)	238 (7)				
$[LNi + H]^+$	210 (100)	210 (100)	272 (67)		240 (35)	
$[LNi - H]^+$	208 (51)	208 (51)				
$[LNi - CN]^+$	183 (1)	183 (1)				
				540 (3)		
			440 (5)			
$[M - C_2H_5OH]^{+\cdot}$					374 (100)	
				365 (2)		
						355 (12)
$[M - C_2H_5OC{=}NH]^+$					348 (12)	
				342 (27)		
			304 (3)			

[a] m/z (relative intensity). [b] Numbering scheme is as identified in Table I; α and β indicate the configuration of the molecular ions, as determined from their MIKE spectra.

The following conclusions can then be drawn (see Table II):

(a) Molecular ions of [Niα_2] and [Niβ_2] exhibit predominantly a β configuration (Scheme II) with traces of the α isomer as proved by intense peaks at m/z 318 in their MIKE spectra.

(b) Molecular ions of [Ni(dbmC_2N_2)$_2$] (**4**) and [Ni(dpmC_2N_2)$_2$] (**6**) are in the α structural ligand configuration, as proved by the MIKE peaks at m/z 555 and 475, respectively.

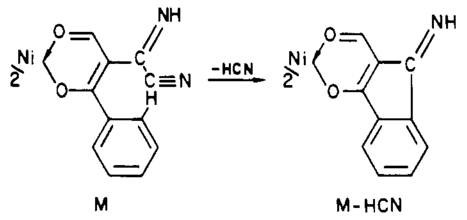
(c) For [Ni(baC_2N_2)$_2$] (**3**) molecular ions the two different forms, i.e. α and β, are present, as shown by the presence of both the peaks at m/z 442 and 431 in its MIKE spectrum.

(d) Finally for [Ni(eaaC_2N_2)$_2$] (**5**) the two peaks at m/z 378 and 348 indicate the presence of the two [Niβ_2]$'$ and [Niβ_2]$''$ structures.

MIKE spectra indicate that HCN loss is the primary decomposition pathway, except for [Ni(dpmC_2N_2)$_2$] (**6**).

The corresponding (M–HCN) ionic species is particularly abundant for [Ni(dbmC_2N_2)$_2$] (**4**) and [Ni(baC_2N_2)$_2$] (**3**), corresponding to the annulation reaction product shown in Scheme III.

Scheme III



This behavior further supports the presence of α species in $M^{+\cdot}$ of these last compounds and can be well explained by the high stability of the radical ions produced.

In spite of the successful solution of the subtle ligand configurational problem discussed here, it was impossible to ascertain by the usual EI or MIKE spectra the α or β nature of the [M(ligand–C_2N_2)$_2$] neutral species in the solid state. It is necessary to emphasize that all data reported in Table II refer to the structure of the analyte as it emerges from the electron-impact source, i.e. from a space in which thermal and collisional events (in the electron beam) can occur. The case

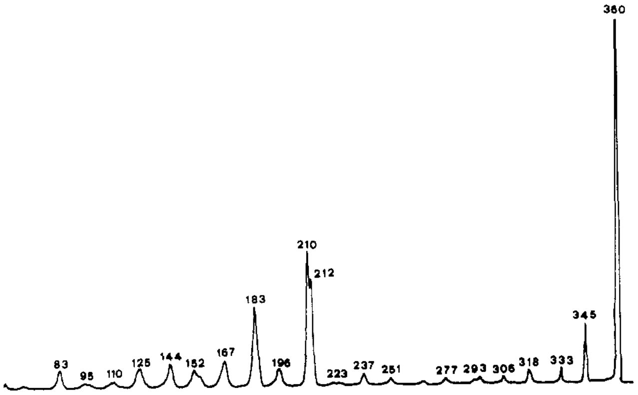


Figure 1. CAD MIKE spectra of [Niα_2] and [Niβ_2].

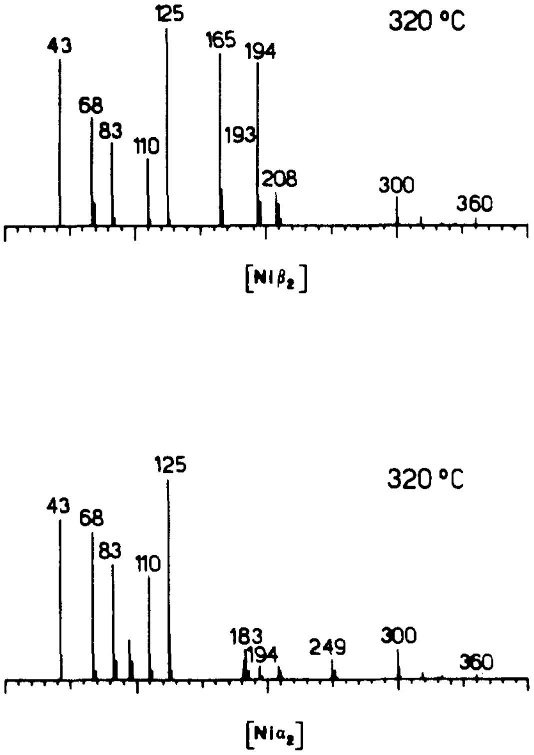


Figure 2. EI spectra of [Niβ_2] and [Niα_2] at 320 °C.

of [Niα_2] and [Niβ_2] is exemplary. We recently demonstrated by DTA-TG measurements[8] that these species are real isomers and not dimorphic phases of the same molecular geometry[1] (even if we could not directly prove the [Niα_2] structure).

The fact that we here demonstrate that both isomers emerge as [Niβ_2]$^{+\cdot}$ from the ion source is a clear indication that although the MIKES technique gives useful information, the analyte may undergo modification during excitation.

CAD MIKE also confirmed the [Niβ_2] nature of the analyte emerging from the ion source: spectra of [Ni(acacC$_2$N$_2$)$_2$] α and β isomers (see Figure 1) are identical, proving definitively that the molecular ions of these two isomers have really the same structure.

The required [Niα_2] → [Niβ_2] isomerization process can originate from (i) thermal processes or (ii) electron-impact-induced isomerization.

In order to shed light on this aspect we have undertaken a series of experiments to delineate the thermal behavior of the two isomers directly in the ion source. The mass spectra of [Niα_2] and [Niβ_2] have been recorded at different ion-source temperatures and at the same low probe temperature (100 °C). The spectra obtained at 320 °C are quite different from each other (Figure 2).

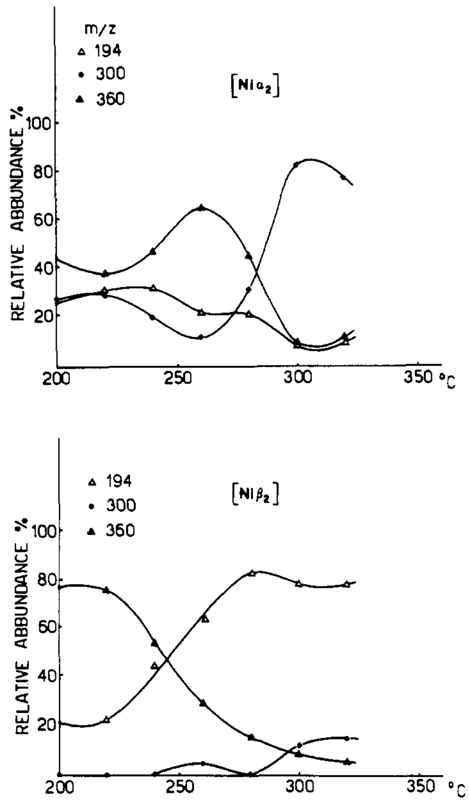


Figure 3. Thermal decomposition pattern of [Niα_2] and [Niβ_2].

The trends of relative abundances of the ions at m/z 360 (M$^{+\cdot}$) and at m/z 300 and 144 (molecular ions of pyrolysis products as shown by linked scans) with ion-source temperature are reported in Figure 3.

These data on thermal behavior can be explained only by considering the existence of two different structures [Niα_2] and [Niβ_2] in the gas phase, which behave differently with the temperature. The obvious conclusion of these results is that [Niα_2] → [Niβ_2] isomerization has to occur in the electron beam.

Experimental Section

All mass spectrometric measurements were performed on a VG ZAB 2F instrument[11] operating in the EI mode (70 eV, 200 μA). Samples were introduced by the DEI technique[12] with a usual ion-source temperature of 200 °C. Metastable transitions were detected by B/E- and B^2/E-linked scans.[13] Collisionally activated decomposition (CAD) mass-analyzed ion kinetic energy spectra (MIKES) were obtained by 8-keV ions colliding with N$_2$ in the second field free region. The pressure of N$_2$ in the collision cell was such as to reduce the beam intensity to 60% of its usual value. Exact mass measurements were performed by the peak-matching technique at 15 000 resolving power (10% valley definition).

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Registry No. **1**, 71616-26-7; **2**, 71616-27-8; **3** ([Niα_2] isomer), 88410-97-3; **3** ([Niβ_2]′ isomer), 93110-79-3; **3** ([Niβ_2]″ isomer), 93134-21-5; **4**, 91886-12-3; **5** ([Niβ_2]′ isomer), 93110-80-6; **5** ([Niβ_2]″ isomer), 93110-81-7; **6**, 87224-95-1.

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(11) Morgan, R. P.; Beynon, J. H.; Bateman, R. H.; Green, B. N. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 171.
(12) Traldi, P.; Vettori, U.; Dragoni, F. *Org. Mass Spectrom.* **1982**, *17*, 581.
(13) Bruins, A. P.; Jennings, K. R.; Evans, F. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 394.