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Negative and Positive Ion Chemical Ionization Mass Spectrometry of Dioximes and their Nickel Complexes

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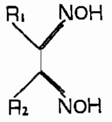
Abstract

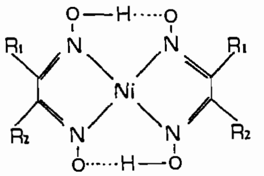
The negative ion mass spectra of $Ni(LH)_2$ (where LH_2 is glyoxime, methylglyoxime, dimethylglyoxime and diphenylglyoxime), in the presence of ammonia or methane at 0.5 torr, are reported and compared with the spectra of the free ligands. In each case, the base peak of the complex is the molecular negative ion and the extent of fragmentation was found to decrease gradually going from the glyoximato to the diphenylglyoximato derivative. In the chemical ionization mass spectra of the free ligands, the $[M]^-$ ion is absent in all cases. The base peak is $[M - H]^-$ for methylglyoximine, dimethylglyoxime and diphenylglyoxime and $[M - H - H_2]^-$ for glyoxime. The fragmentation occurs largely by loss of H, OH, H_2O and NO species. The positive ion chemical ionization mass spectra of the same complexes show very abundant $[M + H]^+$ and $[M]^+$ ions and weak fragments, whilst a rather high fragmentation is observed for the corresponding free ligands.

Introduction

In the past years several mass spectrometric studies have been published on the attachment reactions of low energy electrons on metal-containing compounds and interesting results on the factors affecting the electron withdrawing ability in the gas phase have been described [1–8]. This paper reports on the negative ion mass spectra of the dioximes **1**–**4** and of their nickel complexes **5**–**8** in the presence of ammonia at high pressure. The positive ion mass spectra of the same compounds, in the presence of methane and ammonia at about 0.5 torr, are also reported. The aim is to compare the gas phase behaviour of these nickel dioximato complexes with the corresponding free ligands under chemical ionization conditions.



1-4



5-8

1 and 5 R_1=H, R_2=H
2 and 6 R_1=H, R_2=CH_3
3 and 7 R_1=CH_3, R_2=CH_3
4 and 8 R_1=C_6H_5, R_2=C_6H_5

The electron impact positive and negative ion mass spectra of all these compounds [9] and the chemical

TABLE I. Abundances of the Most Significant Ions in the Negative Ion Chemical Ionization Mass Spectra of LH_2 Compounds[a]

Complexes	Ions							
	$[M - H]^-$	$[M - 2H]^-$	$[M - OH]^-$	$[M - H_2O]^-$	$[M - H - H_2O]^-$	$[M - NO]^-$	$[M - 2H_2O]^-$	$[RCNOH + H]^-$
1	55	3	5	6	100		95	
2	100	25	85	22	85	12		5[b]
3	100	80	64	26	2	7		18
4	100	36	46	56	92	52		15

[a] LH_2 = glyoxime **1**, methylglyoxime **2**, dimethylglyoxime **3**, diphenylglyoxime **4**. [b] Data reported correspond to R = CH_3. The compound also gives analogous ions corresponding to R = H at *m/z* 45 (rel. ab. 8).

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TABLE II. Abundances of the Most Significant Ions in the Negative Ion Chemical Ionization Mass Spectra of $Ni(LH)_2$ Complexes[a]

Complexes	Ions								
	$[M]^-$	$[M-O]^-$	$[M-OH]^-$	$[M-H_2O]^-$	$[M-NO]^-$	$[M+(H_2O+OH)]^-$	$[M-(2H_2O+OH)]^-$	$[M-LH_2]^-$	$[NiN_2O]^-$
5	100	25	19	20	31	26	20	10	15
6	100	5	2	20	5	2	6	3	
7	100	5	3	11					
8	100	2	3	7					

[a] LH_2 = glyoxime 5, methylglyoxime 6, dimethylglyoxime 7, diphenylglyoxime 8.

TABLE III. Abundances of the Most Significant Ions in the Positive Ion Chemical Ionization Mass Spectra of $Ni(LH)_2$ Complexes[a]

Complexes	Ions					
	$[M+H]^+$	$[M]^+$	$[M-H]^+$	$[M-H_2O]^+$	$[M+H-NO]^+$	$[M-L]^+$
5	91	100	4	3	6	7
6	100	58	2	2	1	2
7	100	83		3	2	6
8	100	55		12		

[a] LH_2 = glyoxime 5, dimethylglyoxime 6, dimethylglyoxime 7, diphenylglyoxime 8.

ionization mass spectra of bis(dimethylglyoximato)-nickel(II), with methane as moderating gas [10], have been reported previously.

Results and Discussion

The negative ion chemical ionization mass spectra of the compounds **1**–**4**, in the presence of ammonia, display abundant $[M-H]^-$ ions (Table I). These are the base peaks for **2**, **3** and **4** whilst in the mass spectrum of **1** the most prominent fragments are $[M-H-H_2O]^-$. In all cases no electron capture resonance process takes place to give $[M]^-$, as in the electron impact negative ion spectra [9], suggesting that the oximino group is not so effective in stabilizing the non-dissociative electron capture. This is in contrast to the behaviour of the nitro and nitroso groups linked to aromatic skeletons [11] and also of the carbonyl groups bonded to aromatic or other unsaturated units [12].

However a comparison of the ionic abundances reported in Table I with those displayed by the same compounds in a conventional ion source [9] shows a significantly less pronounced fragmentation of the $[M-H]^-$ ions under chemical ionization conditions. In the presence of NH_3 the dissociative capture process becomes less important due to the reduced excitation of the ionic species, which occurs in the presence of high secondary electron density.

The behaviour of the negative ions in the spectra **1**–**4** appears to be related to the nature of the R and R′ substituents. The percentage of the total ion current transported by $[M-H]^-$ is the lowest in the mass spectrum of **1** and gradually increases passing to **2** and **3**. The aryl substituted compound **4** follows a behaviour intermediate between that of **2** and **3**.

When methane is used as the moderating gas, the negative ion mass spectra of these compounds show the same overall trend of ionic abundances observed with ammonia, but the total ion current is substantially lower.

In the spectra of the nickel dioximato complexes **5**–**8**, in the presence of ammonia, $[M]^-$ is always present as the base peak (Table II). This is to be ascribed to the presence of chelating ligands, which allows the excitation energy to dissipate with the breaking of a metal–ligand bond without any loss of neutral species. In all cases the fragmentation of $[M]^-$ involves loss of O, OH and H_2. In the case of compounds **5** and **6** loss of NO and LH_2 is also observed.

Fragmentation is far more pronounced in the hydrogen substituted compounds **5** and **6**. This can be related to the involvement of the hydrogen substituents in the elimination of OH and H_2. Similar behaviour is shown by bis(salicylaldoximato)nickel(II), which has an aldehydic hydrogen and shows facile loss of OH and H_2 from the molecular ion [9].

The positive ion spectra of the dioximes **2**, **3** and **4** exhibit $[M+H]^+$ as the major ion and $[M]^+$ as the second most abundant ion both in the presence of methane or ammonia at 0.5 torr. For compound **1** this is reversed to give $[M]^+$ as the major ion. The fragmentation of all these compounds is high and leads to low mass fragments for which assignments cannot be made due to overlapping with ions arising from the moderating gas. In contrast the spectra of the respective complexes in the presence of ammonia show little fragmentation with more than 90% of the ion current being carried by $[M + H]^+$ and $[M]^+$ (Table III). Generally fragmentation occurs by loss of OH, NO and the species L.

Experimental

All the compounds were prepared according to the methods reported previously [9].

The mass spectra were run on a double-focusing Kratos MS 80 mass spectrometer of the Laboratory of Gas Chromatography–Mass Spectrometry, Provincia of Turin, University of Turin. Operating conditions were as follows: primary electron energy 60 eV, emission current 500 μA, accelerating voltage 4 kV, resolution 1000 (10% valley definition), scan rate 3 s/dec and reagent gas pressure *ca.* 0.5 torr. The compounds were introduced through a direct insertion probe heated at the minimum temperature necessary to obtain reproducible ion abundances.

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