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STRUCTURE OF A REACTION PRODUCT OF NICKEL ACETYLACETONATE

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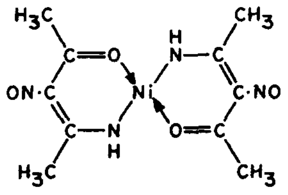
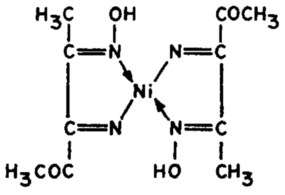
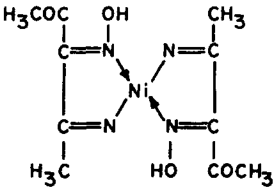
Nickel acetylacetonate has been reported to react with nitrite in presence of ammonium acetate in slightly acidic medium (1,2). The red crystalline compound obtained has been assigned the formula $Ni(C_5H_7N_2O_2)_2$. Structures I and II have been suggested for this compound on the basis of its infrared spectrum. However, mainly on account of the diamagnetism of the compound structure II has been favoured for it, since structure I involves oxygen as one of the donor atoms, and this atom does not readily bring about spin-pairing.



I



II



III

On the basis of mass spectral evidence structure III is now assigned to the compound.

The mass spectrum (FIG.1) of the nickel compound recorded on a model MCH 1303 (USSR) mass spectrometer by the direct introduction of the sample in the ion source showed a very intense molecular ion at m/e 312 (which confirms

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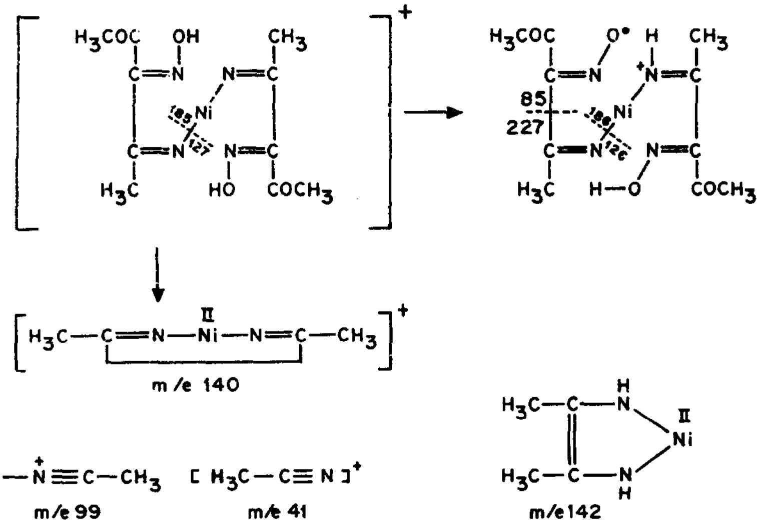
the molecular formula) and the base peak at m/e 99*.

The major peak at m/e 227 appears to be formed by a rearrangement involving the direct loss of 85 mass units ($C_3H_3NO_2$) from the molecular ion. This is supported by the meta-stable peak at m/e 165.5(cal. 165.1).

This rearrangement is followed by a loss of 41 mass units ($CH_3-C\equiv N$) resulting in the fragment with mass 186. Again the meta-stable peak at m/e 152.5 (cal. 152.4) supports this fragmentation mode.

It is difficult to conceive of the successive loss of these two fragments from the molecular ion on the basis of structures I and II. If the compound has structure III and if a proton from the oxime group of one ligand is transferred to the nitrogen atom of the second ligand, the loss of a stable $CH_3-\underset{\overset{\|}{O}}{C}-C\equiv N\rightarrow O$ molecule can be envisaged. The resulting ion can then lose another stable $CH_3-C\equiv N$ molecule. The proton transfer is probably facilitated through a hydrogen bonded structure.



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* The spectrum obtained on an Atlas CH4 mass spectrometer was similar except that the base peak was at m/e 186.

After the hydrogen transfer the molecular ion can lose the remainder of the ligand to give the peak at m/e 126.

The fragments with mass 140 and 142 contain the nickel atom (as is evident from the 'isotopic clusters') and parts of both the ligands.

Under conditions in which the nickel compound is formed from nickel acetylacetonate, nitrosation at the middle carbon atom of acetylacetone is possible (3). If one of the two carbonyl groups is then converted to an imino group, the resulting ligand can form a metal chelate of structure III and not structure II. This is because the acetyl group should be found attached to the carbon atom linked to the oxime nitrogen and not to the imino nitrogen.

For further confirmation of structure III, a comparison was sought with the mass spectrum (FIG.2) of nickel dimethylglyoxime, the structure of which has been firmly established by X-ray crystallography (4). Both of these compounds are diamagnetic and their chelate rings are identically constituted.

Comparison of the mass spectra revealed certain similarity in the fragmentation modes. The common fragments observed in both the spectra are at m/e 99, m/e 116, m/e 140 and m/e 142. These fragments appear to contain nickel.

The fragments with mass 99, 140 and 142 reveal that the molecules have $CH_3\text{-}\underset{|}{C}{=}N\text{-}Ni\text{-}N{=}\underset{|}{C}\text{-}CH_3$ chain present in them. This is present in nickel dimethylglyoxime and only in structure III.

Structure III can equally well explain the infrared spectral data and the diamagnetism of the compound.

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