A Metal Template Rearrangement: Formation of Metal Complexes of 2,2′-Pyridilic Acid

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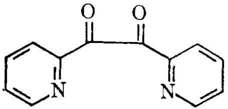
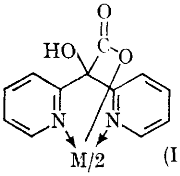
WE report preliminary details for a molecular rearrangement of the benzilic acid type, which is promoted by metal chelation. 2,2′-Pyridil (I) reacts with hydrated nickel or cobalt acetates in methanolic solution forming 2,2′-pyridilic acid metal complexes (II; $M = Ni^{II}$ or Co^{II}) in almost quantitative yield.

Structure (II) has been confirmed for the products by the following evidence. Combustion analysis gave the empirical formula $C_{24}H_{18}N_4O_6M$, showing that two pyridilate anions are attached to one metal cation. The infrared spectra of the nickel and cobalt complexes (II) were essentially identical and showed absorption at 3300 (hydroxyl), 1650 (carboxylate), 1660 and 1575 $cm.^{-1}$ (pyridyl) and other peaks consistent with structure (II). Both compounds (II) were paramagnetic with moments of 3·0 and 4·7 B.M., consistent with octahedral nickel(II) and cobalt(II), respectively. They were also found to be identical with respective authentic 2,2′-pyridilic acid complexes, prepared from sodium 2,2′-pyridilate[1] and metal acetates in methanol. A comparison of the infrared spectra of the sodium, nickel, and cobalt salts shows that the pyridyl groups are co-ordinated[2] in the last two examples, thus confirming the tridentate nature of the pyridilate ligand. Molecular models clearly show that such tridentate behaviour is to be expected. The benzilic acid rearrangement involves base-catalysed hydration of the benzil with simultaneous migration of an aryl group. Usually, strong aqueous alkali or alcoholic alkoxide is required. Aqueous potassium hydroxide[3] decomposes 2,2′-pyridil, but Klosa[1] effected its conversion into the sodium salt of 2,2′-pyridilic acid by boiling with sodium methoxide. Even mild acidification of this sodium salt resulted in decarboxylation and production of 2,2′-dipyridylmethanol, whereas the nickel and cobalt complexes are highly stable, requiring severe acid treatment for decarboxylation.

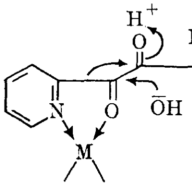
This extremely mild rearrangement is indeed dependent on chelation. Under these conditions, benzil is not rearranged to benzilic acid although it is capable of functioning as a weak bidentate ligand. The conversion of (I) into (II) cannot be achieved by hydrated sodium acetate in methanol. Nickel salts other than acetate have failed to effect the rearrangement under similar conditions, neither have manganese and magnesium acetates. Reaction of hydrated copper(II) acetate with 2,2′-pyridil yielded bis-2-picolinatocopper(II), confirmed by comparison with an authentic sample.



(I)



(II)



(III)

The precise nature of this pyridilic acid rearrangement, schematically shown in structure (III), is now under investigation. It is clear that chelation provides the driving force for this rearrangement by stabilising the product. This phenomenon is now well established[4] and is of great importance in enzymic systems. However, we have described the first example *in vitro* of a molecular rearrangement involving group migration, effected by a metal template.

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[1] J. Klosa, *Naturwiss.*, 1957, **44**, 558; *J. prakt. Chem.*, 1960, **10**, 335.

[2] N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

[3] D. Oda, *J. Chem. Soc. Japan*, 1961, **82**, 478 (*Chem. Abs.*, 1962, **56**, 10089b).

[4] D. St. C. Black and E. Markham, *Rev. Pure. Appl. Chem.* (*Australia*), 1965, **15**, 109.