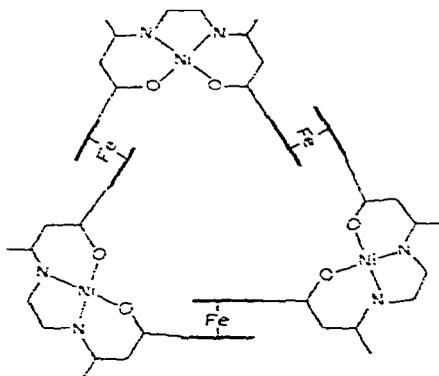


Template synthesis of a novel bimetallic ferrocene-Schiff base complex

Organometallic compounds containing more than one kind of metal ion have been reported¹, and some ferrocene derivatives which contain a dicarbonyl moiety are known to form copper(II)-chelate compounds². It has now been found possible to prepare a novel type of organometallic-metal-chelate compound by means of a template system³. Interaction of a ferrocenebis(β -diketone), 1,1'-(butane-1,3-dione)-ferrocene (I), and a nickel(II) template [μ -dichlorotetrakisethylenediaminedinickel(II) chloride (II), plus pyridine] affords the condensation product, III: cyclo-tris-[*N,N'*-ethylene-1,1'-(butane-3-imino-1-onato)ferrocene nickel(II)] for which a cyclic structure (III) may be proposed. As is typical of a template synthesis the product was obtained in a highly pure state.



III

The identity of the product is indicated by microanalytical data, by molecular weight data, and by infrared spectra. The microanalytical data are in good agreement with the values calculated for complete condensation. The molecular weight (1280, obtained by the Rast method using acridine) is in good agreement with the value calculated for the trimer (1305). The possibility that the product is a mixture of low-molecular weight polymers seems unlikely because incomplete condensation would lead to significant deviations in the percentage composition. The infrared spectrum (Nujol mull) has a set of three bands at 6.10 μ (w), 6.36 μ (s), and 6.56, 6.61 μ (s) which represent a pattern that is typical of β -ketoimine-metal compounds⁴, and which has been ascribed to C...O, C...C, and C...N stretching frequencies. Further, the spectrum lacks a band in the 5.7-5.9 μ region which would be characteristic of a free ketone carbonyl group. The Schiff base formation is presumed to involve the acetyl oxygen instead of the ring conjugated carbonyl because this appears to be the preferred mode of condensation in template syntheses^{3,4}.

Compound III was prepared by the template synthesis: 1,1'-di(1,3-butanediono)-ferrocene (0.35 g, 1 mmole) (Research Organic Chemicals, Sun Valley, California) was added to a solution of μ -dichlorotetrakisethylenediaminedinickel(II) chloride (0.25 g, 0.5 mmole) and 3 drops of pyridine in 200 ml of methanol. The solution was refluxed for 48 h and the dark red crystalline product (0.26 g, 60%, m.p. > 360°) was collected by filtration. (No further purification was necessary.) Found: C, 55.24; H, 4.60; N, 6.44; $C_{20}H_{20}N_2O_2FeNi$ calcd.: C, 55.00; H, 4.50; N, 6.24.

The importance of the template method is seen from the following: Attempts to prepare compound III by constituent combination⁵ (using dilute ethanolic solutions of I, nickel acetate, sodium acetate and ethylenediamine) were unsuccessful. Preliminary attempts to effect condensation of I and ethylenediamine in benzene solution were also unsuccessful. Preliminary studies indicate that the template method can be used to prepare coordination polymers from suitable bis(β -diketones).

The authors acknowledge with gratitude the support of P.H.S. Grant GM 12604-01, Division of General Medical Sciences, U.S. Public Health Service.

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Received November 29th, 1965