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The Reported Synthesis of the Tetraphenyl Tetraazaannulene Macrocycle: 6,8,15,17-Tetraphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecene*

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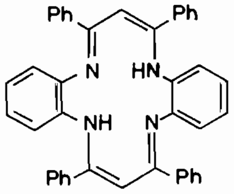
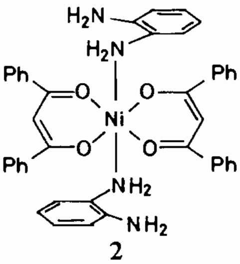
Our recent interest in the electrochemical and potential catalytic properties of tetraazaannulene macrocycles has led us to explore their synthetic chemistry [1]. Of particular interest to us is the synthesis of the tetraphenyl macrocycle, 6,8,15,17-tetraphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecene (**1**).



1

The only iron complexes of macrocyclic ligands that are known have been prepared by complexing iron with previously prepared ligands [2]. As a result, we were surprised by the reported preparation by Malik *et al.* of the Fe(III) complex of **1** via a template synthesis using $FeCl_3$ [3]. This was also the first report in the literature claiming the use of Fe(II) or Fe(III) in a template synthesis. Our attempts to utilize Ni(II), typically a better 'template metal', to prepare the Ni(II) complex of **1** in an analogous manner were unsuccessful apparently due to the steric sensitivity of the reaction [4]. The product obtained was the bis-diamine adduct of the Ni(II) β-diketonate (**2**) [5]. This result, coupled with the minimal characterization presented by Malik *et al.* caused some concern and prompted us to reexamine their initial report. Malik *et al.* based the assignment of the macrocyclic structure on elemental analyses and infrared spectra. Repetition of their work in our laboratory indicates that the 'Fe(III) macrocycle' is in fact a diamine adduct of the Fe(III) β-diketonate (**3**).



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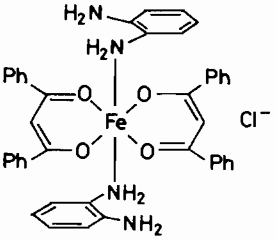

3

The product of the reaction of 1,2-diaminobenzene, 1,3-diphenyl-1,3-propanedione, and $FeCl_3$ in dry methanol does give IR absorbances at 1670, 1600, 1570 cm^{-1} as reported. However, the appearance of an IR absorption near 1650 cm^{-1} and the absence of one around 1700 cm^{-1} does not 'provide conclusive evidence of condensation of the amine with the diketone' as claimed by Malik *et al.* Although C=N stretches of simple imines are generally observed in the range of 1690–1640 cm^{-1} [6], tetraazaannulene macrocycles are highly conjugated systems and conjugation shifts the C=N stretch to lower wavenumbers. Coordination of the imine with a metal ion also shifts the observed stretch to lower wavenumbers. Other tetraazaannulene macrocycles show no infrared absorbances near 1650 cm^{-1} [4, 7]. We attribute the absorption observed at 1670 cm^{-1} to the N–H bend of the uncoordinated $-NH_2$ of the diamine. The 1670 cm^{-1} absorption disappears after washing this complex with CH_3OD, as expected for an N–H bend.

Elemental analysis of the adduct and the 'Fe(III) macrocycle' would be the same within acceptable error limits for C, N, and Fe. The 'Fe(III) macrocycle' should contain three chlorides per molecule whereas the adduct should contain only one. Malik *et al.* did not report the conclusive chloride analysis required. A comparison of the analytical results is presented in Table I.

The observed product in the attempted template condensation of 1,2-diaminobenzene and 1,3-diphenyl-1,3-propanedione with $FeCl_3$ is a diamine adduct of the Fe(III) β-diketonate. The structural assignment is based on infrared spectra, elemental analysis and comparison to the product observed when the same condensation was attempted using

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TABLE I. Analysis of the Diamine Adduct of Fe(III) β-Diketonate

	%C	%H	%N	%Cl	%Fe
Fe(III) macrocycle (calc.)	67.00	4.02	7.44	14.12	7.42
'Fe(III) macrocycle' (found) [3]	66.5	4.1	7.6		7.4
Fe(III) diketonate (calc.)	66.90	5.08	7.43	4.70	7.41
Fe(III) diketonate (found)	67.12	5.06	7.36	4.92	

Ni(II). The IR absorption (1670 cm^{-1}) previously attributed to a C=N stretch has been shown to be a bending mode of an N–H bond. A macrocyclic structure cannot be assigned to this product by analogy to the compound formed by template condensation with 2,4-pentanedione because the bulky phenyl rings of 1,3-diphenyl-1,3-propanedione interfere during the sterically sensitive reaction.

References

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